

Review

A Review on Recent Developments in the Extraction and Identification of Polycyclic Aromatic Hydrocarbons from Environmental Samples

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Abstract: A class of hazardous chemical molecules known as polycyclic aromatic hydrocarbons (PAHs) are frequently detected in environmental samples such as soil, water, and air. Because of their carcinogenic and mutagenic qualities, PAHs pose a significant threat to both human health and the environment. Therefore, the identification and extraction of PAHs from environmental samples is crucial for monitoring and assessing their presence and potential risks. An overview of these recent advancements is given in this review, which includes the use of sophisticated analytical methods for the identification and measurement of PAHs in environmental samples, such as high-performance liquid chromatography (HPLC) and gas chromatography-mass spectrometry (GC-MS). The limitations of conventional extraction techniques such as Soxhlet extraction and liquid-liquid extraction, which are frequently labour-intensive, solvent-intensive, and prone to low selectivity, are highlighted in this review. In contrast, modern techniques such as Solid-Phase Microextraction (SPME) and Accelerated Solvent Extraction (ASE) offer significant advantages, including reduced solvent use, faster processing times, and enhanced sensitivity and selectivity for PAHs. This review highlights the benefits of these advancements in facilitating faster, more accurate, and environmentally friendly PAH extraction and identification processes, focusing on overcoming the limitations of traditional methods such as chromatographic separation and detection. To improve our comprehension of PAH contamination and provide practical mitigation methods for their effects on the environment and human health, this field needs ongoing research and development.

Keywords: extraction methods; PAHs; environmental samples; analytical techniques; water pollution



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1. Introduction

Polycyclic aromatic hydrocarbons are a class of organic chemicals that are ubiquitous in the environment due to their widespread presence in various sources such as industrial processes, combustion emissions and fossil fuels [1–3]. These chemicals have been of particular interest due to their potentially harmful effects on human health and the environment [4]. Significant progress has been made in the detection and extraction of PAHs from environmental samples in recent years [5–9]. Numerous harmful health outcomes, including cancer, aberrant development, and respiratory problems, have been linked to PAH exposure [10,11]. Regulatory bodies such as the Environmental Protection Agency (EPA) have placed restrictions on the permissible quantities of specific PAHs in the environment because of their potential for harm [11,12]. Determining the hazards to human health and implementing efficient pollution management strategies depends heavily on the analysis and monitoring of PAH levels in the environment [10,13–15].

Recent advancements in analytical techniques, such as passive sampling devices and biosensors, have allowed for more efficient and cost-effective detection of PAHs in environmental samples [2,9,16]. These methods offer improved sensitivity and selectivity,

as well as the ability to detect a wider range of PAH compounds [11,15]. Extraction of PAHs from environmental samples is another crucial step in their analysis [8,15]. Traditional extraction methods, such as solid-phase extraction (SPE) and Soxhlet extraction, as well as Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS), have limitations in terms of their effectiveness, reproducibility, and environmental impact [14,16,17]. With less solvent and shorter extraction times, modern extraction techniques including ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE), and ASE offer higher extraction yields [2,12,18,19]. Effectively managing the effects of PAHs in the environment also requires an understanding of their sources and fate [19,20]. Determining PAHs at trace levels in surface waters presents significant analytical challenges due to their low concentrations and the complex matrix of environmental samples [21–23]. The detection often requires highly sensitive techniques such as gas chromatography-tandem mass spectrometry, which can accurately identify and quantify PAHs even at parts-per-billion levels [23].

Moreover, one notable area of advancement is the development of novel extraction methods aimed at improving the recovery and detection of PAHs from complex environmental matrices [20,21,24]. Methods such as liquid-liquid extraction (LLE), ASE and SPME have also been refined to enhance the efficiency of extraction while minimising sample preparation time and solvent consumption [14,17]. Solid-phase microextraction and ASE have emerged as superior alternatives to traditional methods [18,19,25]. SPME provides solvent-free extraction, low sample preparation requirements, and direct coupling with analytical equipment, all of which improve sensitivity and shorten analysis times [7,19]. ASE, on the other hand, uses higher temperatures and pressures to accelerate analyte recovery and solvent penetration, which reduces solvent consumption and shortens extraction durations [20]. These methods are ideal for contemporary PAH analysis since they are more economical and ecologically friendly [7,26,27]. In addition to methodological advancements, there has been significant progress in the development of analytical standards, reference materials, and quality assurance protocols for PAH analysis [4,18]. These efforts have facilitated inter-laboratory comparability and ensured the reliability of PAH measurements, thereby supporting regulatory compliance and risk assessment endeavours [10].

Traditional methods for PAH analysis typically involve sample extraction followed by chromatographic separation and detection [22,28]. However, recent developments in analytical techniques and instrumentation have led to significant advancements in the identification and extraction of PAHs, enabling enhanced sensitivity and efficiency [2,13,29,30]. Conventional methods for identifying PAHs include GC-MS, liquid chromatography-mass spectrometry (LC-MS), and HPLC [8,28]. Nevertheless, these methods can be costly, time-consuming, and require substantial sample volumes [12]. The novelty of this review lies in its comprehensive analysis of the latest advancements in the extraction and identification of PAHs from environmental samples, particularly focusing on emerging techniques such as SPME and ASE. In contrast to previous reviews that focused primarily on old procedures, this work emphasises the drawbacks of traditional chromatographic techniques while highlighting the effectiveness, eco-friendliness, and affordability of modern technologies [11,17,22]. The review also offers a thorough comparison of these contemporary approaches with older ones, showing how they overcome issues with sensitivity, extraction time, and solvent usage [15,16,29].

Overall, continued research in the field of PAH identification and extraction is critical for assessing and mitigating the risks associated with these ubiquitous environmental contaminants [12,30]. By staying informed on the latest advancements in analytical techniques and extraction methods, researchers and policymakers can make informed decisions to protect the environment and human health from the damaging consequences of exposure to PAHs [4,8,31]. The purpose of this review is to provide a broad outline of the most recent achievements in the field, such as new analytical techniques, extraction strategies, and advances in our knowledge of the origins and environmental fate of PAHs. This work will

improve our understanding of the dangers associated with PAH exposure by providing an overview of the present state of knowledge on PAH identification and extraction. It will also help guide future research and policy decisions targeted at reducing these risks.

2. Chemistry of Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons are regularly found in the environment as mixes of two or more compounds, and although they are generally discussed as a category, each constituent is assessed independently to determine risk [9,25,32,33]. This family of compounds contains more than 100 substances, but only a smaller number are frequently recorded at disposal sites [19]. The number and arrangement of aromatic rings in PAHs determine their stability, reactivity, and environmental persistence, among other chemical features [20,21]. It is well known that these substances can undergo processes such as oxidation, nitration, and halogenation to generate derivatives, which can further affect the toxicity and environmental behaviour of these substances [22]. PAHs are very lipophilic but comparatively insoluble in water [23]. In studies on public health and environmental monitoring, PAHs are a major concern because of their mutagenic and carcinogenic qualities [24]. The main physicochemical characteristics of the 16 priority PAHs classified by the United States Environmental Protection Agency are briefly summarised in Table 1, which also includes information on their molecular weight, water solubility, vapour pressure, octanol/water partition coefficient (K_{ow}), and environmental half-life. The K_{ow} , expressed as “log P,” is a critical parameter that indicates the hydrophobicity of PAHs, influencing their environmental behaviour and bioaccumulation potential [34]. A higher log P value suggests that a PAH is more likely to partition into organic phases, such as lipid tissues in organisms, leading to increased persistence and potential toxicity in aquatic environments [34].

Table 1. Key physicochemical properties of the PAHs [25].

PAH	Molecular Weight (g/mol)	Water Solubility (mg/L)	Vapour Pressure (Pa)	Octanol/Water Partition Coefficient (log P K_{ow})	Half-Life (Days)
Naphthalene	128.17	31.7	11.0	3.37	1–3
Acenaphthylene	152.20	3.93	0.6	4.00	3–10
Acenaphthene	154.21	3.8	0.3	3.92	3–10
Fluorene	166.23	1.9	0.03	4.18	3–10
Phenanthrene	178.24	1.1	0.01	4.57	16–126
Anthracene	178.24	0.045	0.01	4.54	16–126
Fluoranthene	202.26	0.26	0.001	5.22	16–126
Pyrene	202.26	0.135	0.001	5.18	16–126
Benz[a]anthracene	228.29	0.014	0.0002	5.91	16–126
Chrysene	228.29	0.002	0.00009	5.91	16–126
Benzo[b]fluoranthene	252.31	0.0015	0.0001	5.80	16–126
Benzo[k]fluoranthene	252.31	0.0008	0.00008	6.00	16–126
Benzo[a]pyrene	252.31	0.0038	0.00005	6.04	16–126
Indeno [1,2,3-cd]pyrene	276.34	0.062	0.000001	6.58	16–126
Dibenz[a,h]anthracene	278.35	0.0005	0.000005	6.75	16–126
Benzo[g,h,i]perylene	276.34	0.00026	0.00001	6.50	16–126

3. Characteristics of Polycyclic Aromatic Hydrocarbons

PAHs are typically solid white, light yellow or colourless substances at room temperature [26]. Poor vapour pressure, extremely poor water solubility, high melting and boiling temperatures and a tendency to decrease with increasing molecular weight are typical

properties [4,27]. Moreover, PAHs vary in how they behave, where they are found in the environment, and how they affect biological systems [30]. These compounds have high lipophilicity, making them very soluble in a wide range of organic solvents [28]. When the molecular weight of PAHs increases, their chemical and physical characteristics are enhanced as well [29]. As such, they can broadly be organised into two categories: Lower Molecular Weight (LMW) and High Molecular Weight (HMW). Their potential effects, therefore, differ as well; for example, LMW PAHs are acutely hazardous to aquatic life, although High Molecular Weight (HMW) PAHs (such as those with four to seven rings) usually are not [31]. On the other hand, it has been discovered that certain HMW substances cause cancer [14,32].

PAHs are considered chemically stable and poorly hydrolysed due to their non-polar, organic nature [33,34]. This is probably because of their extreme lipophilicity and hydrophobicity [1]. According to a number of studies, the dense cloud of pi electrons that surrounds the patterned structure on both sides may contribute to the biological endurance of PAHs and make them extremely resistant to nucleophilic assault [6,10,35]. Some of the PAHs have been found to be susceptible to oxidation and photodegradation in aqueous environments, as determined by the substrates to which they are attached [36,37]. The 16 priority PAHs on the United States Environmental Protection Agency (USEPA) list are depicted in Figure 1.

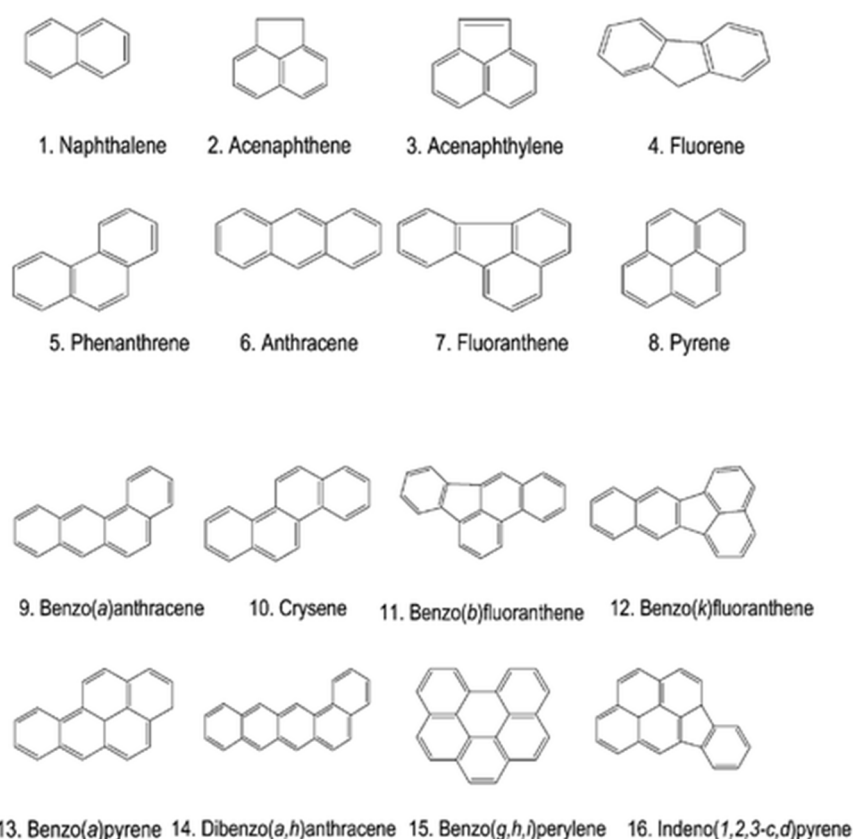


Figure 1. The 16 PAHs listed as priorities by the USEPA [37].

4. Possible Risks Linked to Polycyclic Aromatic Hydrocarbons

It is critical to create regulations to limit the exposure of humans and animals to PAHs due to their mutagenicity, carcinogenicity, and ubiquity in the atmosphere and environment [38,39]. Although there are links between certain PAHs and human cancer that have been established by epidemiological studies on worker exposure to PAH mixtures, these chemicals mostly function as indicators of exposure to the full PAH mixture [40]. Furthermore, results from animal studies are the only available toxicological data used to

assess the carcinogenic potential of specific PAHs, and they are extrapolated to the relatively low levels of exposure that people experience [17,28,41]. This probably makes it more difficult to assess health consequences and assign them to specific PAH components [37,42]. There is no known level of absolute safety for PAH exposure because most of them are genotoxic carcinogens [9].

Dietary consumption has been found to be the main way that humans are exposed to PAHs, with the exception of smoking and populations with occupational exposure [41]. Fruits, vegetables, and crops cultivated in contaminated environments may become contaminated and include some of the PAHs found in food [9]. Additionally, these PAHs build up concentrations in marine creatures that are higher than those in the surrounding environment, primarily in bivalve molluscs [43]. The possibility of exposure to harmful substances such as PAHs is a serious worry when consuming seafood on a regular basis [41]. Certain segments of the population may thus be more vulnerable to PAH exposure through diet [38]. Many epidemiologic studies conducted in recent years have reported that dietary factors are responsible for a significant fraction of human malignancies, including lung and prostate cancers [28,41,44]. Maximum allowed levels have been determined, especially for those PAHs that have been identified as hazardous, carcinogenic, and priority pollutants, since PAHs are a serious problem [45,46]. The maximum allowable levels of PAHs in soil and water samples are shown in Table 2, which is based on data from the USEPA and the Agency for Toxic Substance and Disease Registry (ATSDR).

Table 2. PAHs' maximum permitted concentrations (MACs) in soil and water [46].

PAHs	ATSDR Soil (mg/kg)	ATSDR Water (mg/L)	USEPA Water (mg/L)
Naphthalene	1.0	3.0	–
Acenaphthene	3.0	3.0	–
Acenaphthylene	3.0	3.0	–
Fluorene	3.0	0.005	–
Phenanthrene	3.0	3.0	–
Anthracene	3.0	3.0	–
Fluoranthene	3.0	3.0	–
Pyrene	3.0	3.0	–
Benzo (a) anthracene	0.15	0.005	0.001
Chrysene	–	–	0.002
Benzo (b) fluoranthene	0.3	0.005	0.004
Benzo (k) fluoranthene	–	–	0.002
Benzo(a) pyrene	0.3	0.005	–
Indeno[1,2,3-ghi]pyrene	0.3	0.005	0.004
Dibenzo (a) anthracene	0.3	3.0	0.004
Benzo[hgi]perylene	3.0	3.0	–

5. Formation of Polycyclic Aromatic Hydrocarbons

The pyrolysis of organic compounds at high temperatures, the pyrolysis of sedimentary organic compounds at low to moderate temperatures to produce fossil fuels, and direct biosynthesis by microorganisms and plants are some of the environmental processes that can lead to the formation of PAHs [33,47]. Anthropogenic (human-caused) sources of particulate matter emissions include incomplete organic combustion by-products from burning and cooking, as well as industrial and vehicle emissions from diesel and petroleum-powered engines [33,48]. Naturally occurring volcanoes and forest fires can also produce PAHs [42]. It has been discovered that petroleum hydrocarbons, which are released into the

environment either accidentally or on purpose, are the source of benzo(a)pyrene and other PAHs [36]. Figure 2 shows the formation mechanism of PAHs. The process, which begins with the incomplete burning of organic matter and proceeds to the synthesis of smaller hydrocarbons, their fusing into bigger ring structures, and ultimately the formation of PAH molecules, is visually represented.

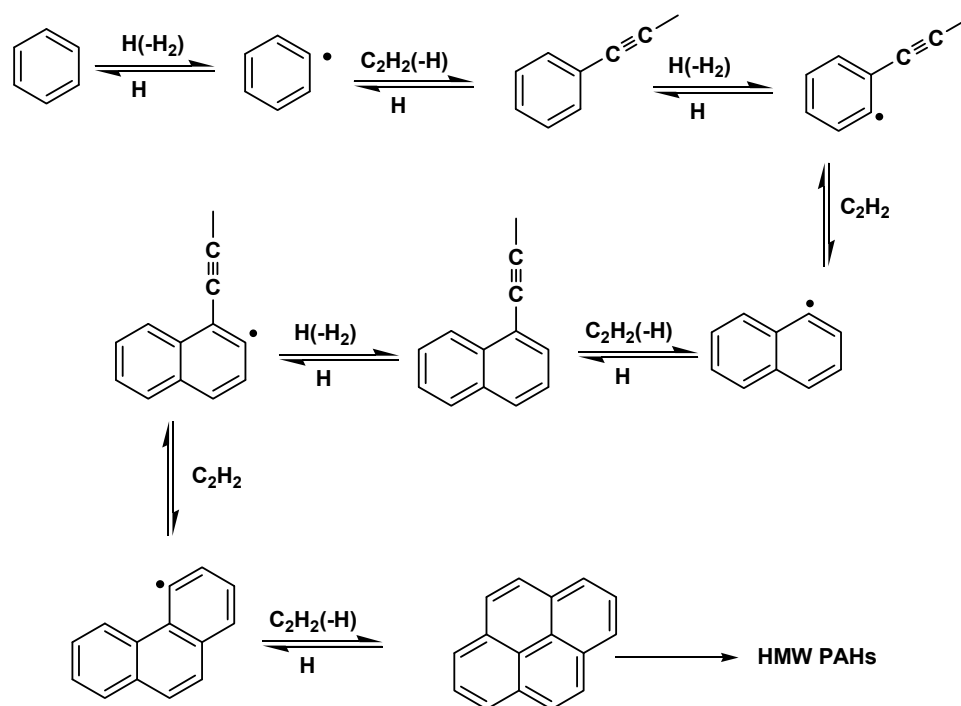


Figure 2. Diagram illustrating the formation mechanism of PAHs.

6. Sources of Polycyclic Aromatic Hydrocarbons

6.1. Anthropogenic and Natural Sources

PAHs mostly originate from two sources: natural and human [33]. During forest fires and volcanic eruptions, incomplete burning of organic materials is one of the natural sources of PAH emissions into the atmosphere [6,33]. Nonetheless, the main cause of PAH pollution is human activity [9]. The primary man-made sources include the combustion of fossil fuels and manufacturing operations [5,33,49]. In addition, the manufacture and usage of asphalt, trash incineration, and tobacco smoke all result in PAH emissions. They are also a result of industrial operations such as the refining of petroleum, the fabrication of coke, and the production of aluminium [50]. Comprehending these multifaceted origins is vital in formulating approaches to alleviate PAH contamination and its correlated health hazards [9].

6.2. Petrogenic Sources

Petroleum-related sources include fuels and other petroleum-derived products such as crude oil [36]. It is well known that petroleum is a complex mixture of many organic chemicals that form in the earth's crust [20,51]. The aquatic environment is exposed to petroleum-based PAHs due to inadvertent oil spills and runoff from cities [33]. The majority of PAHs generated from petroleum have low molecular weight and have two or three rings [1]. Concentrations lower than 100 mg/kg are usually seen for the higher molecular weight fractions [52]. The same PAHs found in the source petroleum are present in these products, along with trace levels that might be created during catalytic cracking and other refining procedures [23]. The range of temperatures at which the product is distilled determines the presence or absence of PAHs in various refined oils [6].

6.3. Pyrogenic Sources

Organic material that has not burned completely is linked to pyrogenic PAHs [33]. Heat causes molecules to break apart when combustion is complete, creating water and carbon dioxide [16]. Additionally, tiny organic compounds may concentrate until new chemicals, such as PAHs, are generated when combustion is incomplete [27]. In homes and businesses, burning or cooking food, as well as the exhaust from diesel and petroleum-powered cars, are examples of human activities that typically result in the production of PAHs [33]. The majority of pyrogenic sources of PAHs are complex, consisting primarily of four, five, and six rings [9].

7. Source Identification and Apportionment of Polycyclic Aromatic Hydrocarbons

Several basic techniques may be applied in the process of identifying and apportioning pollution sources from the environment [53,54]. Of these, receptor models and diagnostic ratios are the two most useful methods that are used [1,50,55]. Because of the varying conditions under which they originate, it is typical to expect different ratios of distinct PAHs depending on the source [1]. Receptor models, which are extensively employed in source apportionment, evaluate the contributions from all significant sources [43,56]. Factor analysis with nonnegative constraints (FA-NNC) is one of the most advanced receptor models and has been successfully used to assess organic pollutants in a range of environmental media, including soils and sediments [16]. Higher molecular weight compounds are more likely to be present in samples containing pyrogenic PAHs than lower molecular weight compounds are in samples containing petrogenic PAHs [1]. High molecular weight PAHs are frequently produced in large quantities during high-temperature combustion activities, which is representative of the global PAH profile. Ma et al. [53] stated that one especially helpful technique for identifying the source of PAHs in soil samples is the diagnostic ratio [53]. The range of diagnostic ratios for the petrogenic and pyrogenic sources of PAHs is shown in Table 3.

Table 3. The variety of PAH source diagnostic ratios [1].

	(LMW PAHs) /(HMW PAHs)	Ant /(Phe + Ant)	Fln /(Fln + Pyr)
Petrogenic origin	>1	<0.1	<0.4
Pyrolytic origin	<1	>0.1	>0.4

8. Polycyclic Aromatic Hydrocarbons as Environmental Pollutants

The persistent presence of PAHs in the environment has been caused by the incomplete combustion of organic waste [57]. In terms of microbes, the majority of PAHs are extremely harmful, carcinogenic, and mutagenic [58]. Another well-known characteristic of PAHs is that they linger in the environment over extended periods of time [13,59]. According to a study by Nemirovskaya [60], PAHs are regarded as the hydrocarbon family's most hazardous contaminants [47]. Hazardous compounds may build up in the food chain as a result, and in certain cases, this may cause major health issues and hereditary illnesses [38]. Combinations, as opposed to single PAHs, account for the bulk of interactions between PAHs in the environment, which can intensify the effects of PAHs that are carcinogenic [60]. Figure 3 shows a simple visual representation of the movement and impacts of PAHs in several environmental compartments, such as the soil, water, atmosphere, and living organisms. Subsequently, PAHs may undergo several processes, such as leaching into groundwater, plant absorption, and degradation [6]. Additionally, they could be consumed via contaminated food or water or inhaled by living things, exposing people and animals. In addition, PAHs have the ability to travel great distances and volatilise back into the atmosphere, which perpetuates the cycle of environmental dispersal [61].

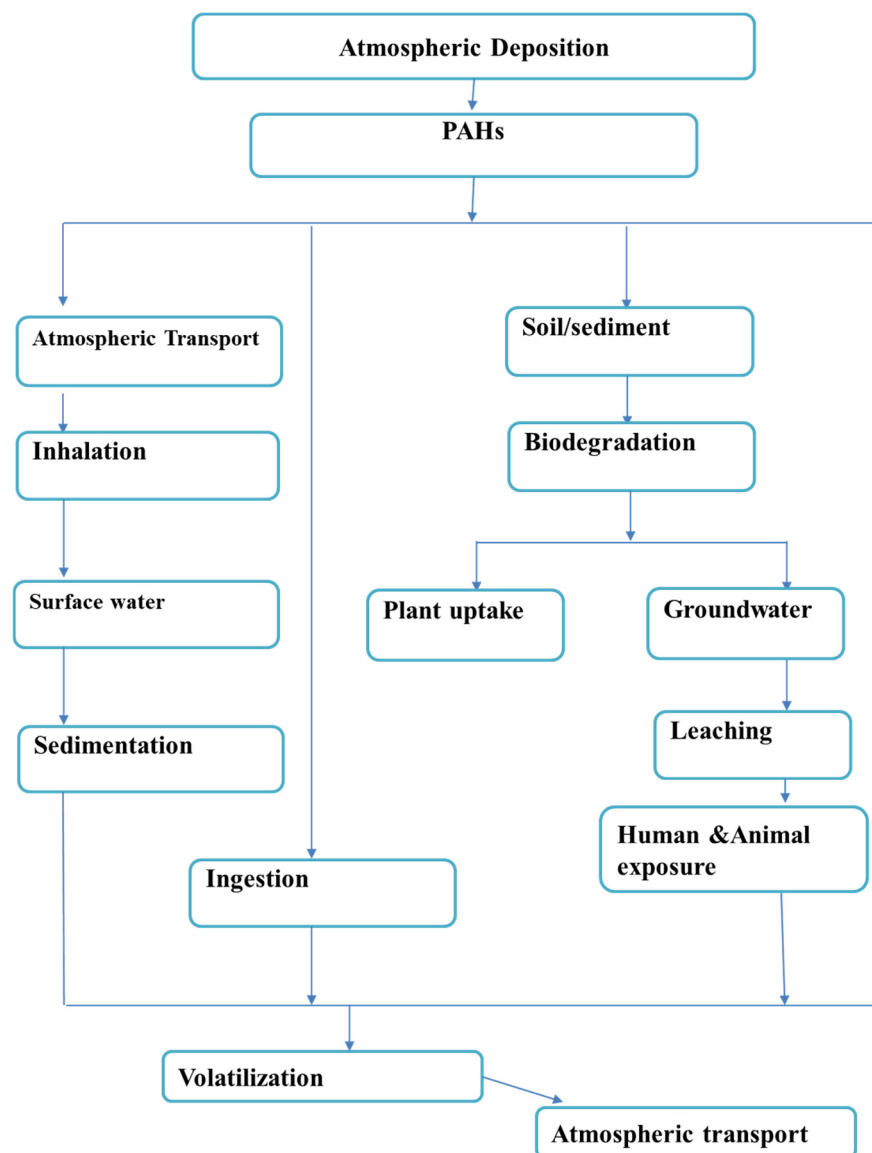


Figure 3. Diagram displaying the environmental fate of PAHs.

8.1. Polycyclic Aromatic Hydrocarbons in Water

Owing to their limited solubility and propensity to bind to particulate matter, aquatic bodies typically contain modest concentrations of PAHs [62,63]. PAH levels in water have been measured in wastewater from North American and European cities, revealing concentrations between <1 and $625 \mu\text{g/L}$, and marine waters, where levels range from non-detected to $11 \mu\text{g/L}$ [64]. The levels of PAH pollution in water from the Loskop Dam and its tributaries were likewise determined by Seopela et al. [64], with amounts ranging from 1.17 to $14.5 \mu\text{g/L}$ [65]. According to Mogashane et al. [26], the Mokolo River had PAH values ranging from 0.0219 to $1.53 \mu\text{g/L}$, while the Blood River had lower quantities (0.0121 to $0.433 \mu\text{g/L}$) [17]. According to a 2003 study conducted by the World Health Organisation (WHO), waters (coastal and surface) normally contain $0.05 \mu\text{g/L}$ of individual PAHs; values higher than this suggest some level of pollution [62]. Research carried out in four major American cities revealed that the overall levels of persistent organic pollutants in clean water varied from 4.7 to $600 \mu\text{g/L}$ [62,65]. Notably, water samples did not contain high molecular mass PAHs. This might be because of their low solubility in water [66].

A study by Ngubo et al. [67] evaluated SPE and ultrasonic extraction (UE) techniques followed by four qualitative and quantitative analyses of PAHs in water and sediment

samples [67]. The percentage of PAHs recovered ranged from 82 to 117% in sediment samples and 85 to 121% in water samples. The ranges of the limits of detection and limits of quantification for SPE and UE, respectively, were 0.02 to 0.2 and 0.05 to 0.5 µg/L and 0.02–0.30 µg/kg, respectively. In wastewater, river water, and dam water, respectively, the concentration levels of PAHs (naphthalene, acenaphthene, acenaphthylene, fluorine, anthracene, phenanthrene, and pyrene) were found to be 0.071–2.7, 2.0–10.4, and 2.5–3.5 µg/L [67].

8.2. Polycyclic Aromatic Hydrocarbons in Sediments

A number of variables, including the makeup of the sediment, the amount of organic matter, the dynamics of water movement, and the existence of microbes that can break down PAHs, affect the analysis of PAHs in sediments [2]. Because of their higher adsorption capability, fine-grained sediments with high organic content typically have greater amounts of PAHs [8]. However, the chemical form of PAHs and the surrounding environment determine their bioavailability and toxicity in sediments [9]. Benthic species are susceptible to harmful effects and probable biomagnification across the food web due to the accumulation of PAHs in their tissues [67]. Therefore, sediments containing these compounds constitute a concern to these animals [6,67]. In order to control and lessen the effects of PAHs on aquatic ecosystems and sediment quality and to safeguard human health and biodiversity, regular monitoring and regulatory frameworks are essential [68,69]. Sediments typically contain higher concentrations of PAHs than water [9,70]. The proportion of PAHs in soil and sediment can reveal information about their presence in the environment, according to research by Chen et al. [71]. The capacity of PAHs to adsorb to dust particles and settle in sediments is the cause of this [71]. Sediment core research indicates that during the preceding 90–150 years, PAH contents have increased [72]. A study by Seopela et al. [64] found that the quantities of PAH in the sediments of the Loskop Dam ranged from 292 to 2170 µg/kg [65]. Another study by Kariyawasam et al. [2] compared the extraction techniques for the analysis of PAHs in sediment and soil samples [2]. The techniques yielded similar PAH recoveries, with >80% of applied pyrene, chrysene, and benzo[a]pyrene being recovered [2].

8.3. Polycyclic Aromatic Hydrocarbons in Air

Biological resources, soil, water, and sediment all receive PAH deposition from the atmosphere [44]. There is a wide range in the measured levels of PAHs in the atmosphere, with urban areas having the highest levels because of diesel engine use and intensive traffic [10]. In addition, there are higher concentrations of PAHs in the air in places where coal, tyres, or agricultural crops are burned, as well as in industries that produce coal tar, roast coal, or operate smokehouses [41]. As a result of lower thermal and photodecomposition as well as combustion products from heating, wintertime air concentrations of PAHs are often greater [71]. Furthermore, smoking raises one's daily personal exposure to PAHs [41]. The typical ratio of PAHs in the atmosphere polluted by industrial emissions, vehicles and heating systems varied from 3.7 to 450 ng/m³ [19]. There are both gaseous and particle forms of PAHs in the atmosphere, with the majority being present in the particulate phase at room temperature [56]. The vapour pressure of each individual PAH determines how it separates into the gas and particle phases [16].

Ma et al. [61] examined changes in the Bohai Sea's atmospheric PAH concentrations, sources, health risks, and direct medical expenses related to lung cancer against the backdrop of China's efforts to prevent and regulate pollution [61]. In order to understand the fluctuation in concentrations and sources, PAH levels were measured in air samples. The health risks and direct medical expenses related to lung cancer brought on by PAH exposure were also calculated in the study [61]. As a consequence of the shift in LMW-PAH concentration, PAH concentrations were often highest in the winter and lowest in the summer. This study demonstrated how efficiently enforcing pollution prevention and

control can lower the concentration of pollutants, the risks they provide, and the medical expenses related to diseases brought on by the corresponding exposure to pollutants [61].

8.4. Polycyclic Aromatic Hydrocarbons in Soil

PAHs have a propensity to bind tightly to organic matter and small particles once they are in the soil, which reduces their ability to degrade, increasing the likelihood of long-term persistence [2,73]. Variations in soil type, temperature, microbial activity, and the presence of other contaminants all affect the distribution of PAHs in soil [36]. Since high concentrations of PAHs in soil can be absorbed by plants, seep into groundwater, and be inhaled or consumed by people and animals, they can be hazardous to both the environment and human health [15,74]. Identification of the sources and levels of contamination, assessment of possible exposure routes, and application of remediation techniques are all necessary steps in the assessment and management of PAH contamination in soil [28]. Soil cleaning, thermal desorption, phytoremediation, and bioremediation are examples of common remediation processes [2,9]. To reduce the negative effects of PAHs on soil quality, protect ecosystems, and safeguard public health, regular monitoring and regulatory actions are crucial [74]. According to Wick et al. [75], the levels of PAHs in Welsh soils exhibited a range of 0.1 to 55 mg/kg, even in the absence of direct industrial pollution [73]. A study by Liu et al. [9] evaluated PAHs in Taiyuan City's plain and mountain soil, investigating concentrations, distribution, sources, and carcinogenic risk [9]. The study found that 4-ring and 5-ring PAHs were more common in plain soil, whereas 2-ring and 3-ring PAHs were more common in mountain soil. The central-north of Taiyuan was found to be the most polluted location, with higher concentrations seen in areas near industrial or business sectors [9]. These results emphasise the necessity of improving urban environmental quality while taking PAH contamination into account. The recovery rates of spiked PAHs standard ranged from 82% to 114%, according to their preliminary recovery testing [9].

8.5. Polycyclic Aromatic Hydrocarbons in Plants

PAHs can be absorbed by plants through their roots from contaminated soil or water and through their leaves from the atmosphere [48,75]. There are concerns about the possible effects of PAHs on plant health and their propensity to enter the food chain [76,77]. Herbivores and people who eat these plants are at risk because PAHs can move to other parts of the plant once they are absorbed, such as the leaves, stems, and fruits [28]. Phytotoxic effects caused by PAHs, including decreased growth, poor photosynthesis, and oxidative stress, can adversely affect plant health and yield [35]. The main causes of PAH build-up in vegetation are atmospheric fallout and absorption by above-ground plant components [75]. In non-industrialised areas, plant tissues usually contain 50–80 µg/kg of PAHs, though this might vary depending on the type of plant, the type of PAH, and the surrounding circumstances [75].

Because of a variety of industrial operations, urban vegetation frequently contains higher amounts of PAHs than vegetation found in rural areas [6,38]. However, because plants cannot transport hydrophobic compounds such as PAHs in the xylem, they are typically adsorbed into the roots but are not translocated to the above-ground sections [16]. The main sources of PAHs in food are contaminated soil used for crop or plant cultivation, or improper processing techniques [75]. A study by Woźniak et al. [78] assessed PAHs in herbal plants collected from three different backyard gardens in Poland [78]. The data obtained indicate that the species and cultivation site of herbs have an impact on the degree and composition of plant contamination with PAHs [79]. Facilities in the mining and energy sectors, in particular, are known to be producers of PAHs, which contaminate plant material intended for direct use or for use in bioactive herbal extracts [78].

8.6. Polycyclic Aromatic Hydrocarbons in Humans

The most common pathways of human exposure to PAHs are eating and drinking, skin contact with soil, inhaling airborne particles of dust and soil, and re-suspended dust

and soil [14]. These sources are pertinent worldwide [36]. Soil interaction typically occurs outdoors, inhalation takes place both indoors and outdoors [52], and food and water consumption often occurs indoors [6]. When breathing in air that contains PAHs, the chemicals can enter the human body through the lungs. PAHs can be found in smoke from a variety of industrial locations, wood, coal, and cigarette smoke [9]. Living close to a hazardous waste site increases the risk of exposure from breathing in PAH-containing air [28]. The rate and extent to which lungs can absorb PAHs, however, remains unknown [39]. If skin comes into contact with high-PAH soil under typical environmental exposure settings, PAHs may enter the human body [6]. The European Union has established permissible limits for PAHs in food, such as a maximum of 10 µg/kg for the sum of four key PAHs (benzo[a]pyrene, benz[a]anthracene, benzo[b]fluoranthene, and chrysene) in processed products [80]. These limits are set to minimise exposure to these carcinogenic compounds and protect public health [80–82].

9. Extraction Techniques

9.1. Liquid-Liquid Extraction

PAHs can be extracted from water using a process called liquid-liquid extraction [63,76]. To achieve this, aqueous samples are separated from the PAHs by placing them in an immiscible organic solvent [17,83,84]. Dichloromethane, hexane, and toluene are common solvents because they are non-polar and have a high affinity for PAHs [77]. Good solvent properties for LLE are generally thought to include low viscosity, high solute solubility and low carrier liquid solubility, density difference, high resistance to heat degradation, and high boiling point [11]. As a result, it is frequently employed in applications that call for the high extraction efficiency determination of chemicals with varied polarity [65]. Dichloromethane is used as the extraction solvent in the standard EPA Method 610 to remove PAHs from water using liquid partitioning [19].

LLE is preferred for its simplicity, effectiveness, and capacity to handle large volumes of water samples; however, it requires careful handling of organic solvents and consideration of their environmental impact [11,78]. LLE offers the advantage of being a simple and cost-effective method for separating and concentrating PAHs from environmental samples, particularly when dealing with large volumes of water [12,25]. Its primary drawbacks, however, include the possibility of incomplete phase separation, which can result in reduced extraction efficiency, and the usage of substantial volumes of organic solvents that may be dangerous [12,18]. To obtain sufficient recovery of the target chemicals, LLE can also be time-consuming and necessitate several extraction procedures [44].

In order to maximise the recovery of PAHs from water samples and guarantee reliable analytical results, it is imperative to optimise the extraction conditions, including solvent type, volume ratio, and extraction time [11]. Repeated extractions with fresh portions of the organic solvent may be carried out to enhance extraction efficiency [17]. After combining the obtained organic extracts, any leftover water is dried over anhydrous sodium sulphate, and the mixture is concentrated by evaporation under low pressure [77]. Using LLE, Nekhavhambe et al. [85] extracted PAHs using dichloromethane as the solvent, yielding individual PAH levels that ranged from 0.1 µg/L to 137 µg/L [63].

Mogashane et al. [26] conducted a study on the identification of 16 PAHs in water samples. The extraction of PAHs from water was accomplished using the LLE method. Using a gas chromatograph-flame ionisation detector, 16 PAHs were quantified in the water [17]. The efficiency and precision of the PAH extraction method were ascertained. All of the compounds had higher percentage recoveries (over 81%), with the exception of Nap and DahAnt, which had percentage recoveries of 67.6 and 75.2%, respectively [17].

9.2. Microwave-Assisted Extraction

The most recent technique for efficiently removing PAHs from a range of matrices, including biological tissues, soils, and sediments, is microwave-assisted extraction [2]. Using microwave energy to rapidly heat the sample and solvent, MAE significantly enhances

the extraction process compared to conventional techniques [2,8]. MAE offers various advantages over standard extraction procedures, including decreased extraction times, lower solvent usage, and improved extraction efficiency [1,15]. Additionally, the closed-vessel method employed in MAE decreases the loss of volatile components and allows better control over the extraction conditions [15]. When extracting PAHs from intricate matrices, where more traditional methods might be inefficient or time-consuming, this technique comes in handy [16]. Because of its efficiency and reproducibility, MAE is a useful tool in environmental analysis [8]. It can quickly and accurately determine the presence of PAHs in a variety of sample types while using less solvent, which has a minimal negative impact on the environment [2].

MAE is less expensive than supercritical fluid extraction [8]. The principal limitation of this method is the requirement for the solvent to be physically separated from the sample matrix in order to perform further analysis after PAH extraction [2,15]. This method produces a cleaner, less contaminated extract faster than other methods, increasing the accuracy of analysis that comes after [8]. Since it provides a dependable and repeatable technique for assessing PAH contamination in sediments, MAE is very useful in environmental monitoring and remediation investigations [2]. Mekonnen et al. [50] extracted PAHs from sediments by means of MAE with a mixture of n-hexane and acetone (1:1, *v/v*) [34]. Similar to this, Seopela et al. [64] extracted all of the PAH content from sediments using MAE and a combination of acetone and hexane, yielding values that ranged from 292 to 2170 µg/kg [65].

Liu et al. [9] conducted a study on the determination, sources, and health risk assessment of PAHs in urban soils using MAE. Their study evaluated the levels, sources, and carcinogenic potential of PAHs in the plain and mountain soil in Taiyuan City. It was established that the main source of PAHs was coal burning [9]. The city's overall PAH-related cancer risks were found to be minimal, according to incremental lifetime cancer risks (ILCRs); nevertheless, locations that were severely contaminated exhibited intermediate threats. These results emphasise the necessity of taking PAH contamination into account while improving the quality of the urban environment [9].

9.3. Mechanical Agitation

Polycyclic aromatic hydrocarbons can be extracted from sediment samples using a straightforward, inexpensive method called mechanical shaking [6,8]. This technique uses a magnetic stirrer dipped straight into the solution, or it uses agitation or mixing in a shake-flask mounted on a rotary shaker [9]. This approach has not been frequently employed since, when compared to Soxhlet and sonication methods, it produces less satisfactory quantitative findings and uses less glassware and extraction solvent in smaller amounts [80]. Mechanical shaking, on the other hand, has been compared in several studies to the Soxhlet method; however, the results of this method showed greater fluctuations and less selectivity, which made it challenging to quantify PAH extracts [6,19]. Extensive shaking durations were necessary to attain similar outcomes and prolong the solvent contact period [8,81].

Mogashane et al. [8] conducted a study comparing extraction methods for the analysis of PAHs. The aim of their investigation was to assess and improve three distinct extraction methods for the detection of PAHs in sediment samples [8]. The MAE was chosen for the extraction of PAHs from sediment samples due to its better extraction effectiveness (>80%) and greater precision as compared to ultrasonication and the combination of ultrasonication and mechanical agitation, which showed low precision. However, further preparations such as extract filtration or centrifugation are needed before using mechanical agitation [8]. Reports that have been published indicate that compared to Soxhlet or ultrasonication procedures, mechanical agitation produces a lower extraction efficiency of PAHs (<75%) [80,81].

9.4. Ultrasonication

When compared to reflux approaches, ultrasonication is a more effective method to extract PAHs from soils and sediments [8,15]. Compared to other extraction approaches, ultrasonic methods have been demonstrated to produce PAHs in amounts that are equivalent or even higher [15]. However, Kumar et al. [86] and Mogashane et al. [8] have shown poorer recoveries when utilising this approach in their investigations [8,86]. The sample-solvent mixture can be agitated by submerging it straight into a sonication bath. Sonication is a better option than Soxhlet because of its easier operation and higher extraction efficiency [15]. Kumar et al. [86] and Mogashane et al. [8] observed that, like with the Soxhlet extraction method, high sonication can yield extraction efficiencies comparable to those attained [8,86]. However, the sample matrix and the amount of contaminants in the sample have a significant impact on the extraction efficiency [80].

In contrast to these findings, additional research has shown that Soxhlet is more effective than sonication, especially when it comes to lower molecular weight PAHs and relatively modest recoveries [8]. According to Oluseyi et al. [70], extended exposure to radiation can degrade pollutants in the sample and decrease the extraction effectiveness of PAHs; hence, it is important to properly control the duration of sonication [70]. Because of an increase in fragmented carbonaceous particles and an increase in adsorption surface area, excessive sonication can reduce efficiency and create a reversed adsorption cycle for PAHs [70]. Furthermore, following the extraction procedure, additional separation methods such as centrifugation or filtration are frequently needed [8,87,88].

Doong et al. [81] carried out a study on the optimisation of ultrasonication extraction for the identification of PAHs in air particles. Under both controlled and uncontrolled ultrasonication temperatures (25–28 °C), ultrasonication extraction was done in the dark. All of the studies used the same special extraction time of 20 min [81]. The results showed that utilising dichloromethane as the extraction solvent in the dark at an ultrasonication temperature of 25 to 28 °C resulted in a noteworthy proportion of PAH recovery (82–108%). The accuracy of the sample analysis was validated by the ultrasonication extraction method, which revealed good reproducibility with a relative standard deviation of PAHs below 6.14%. The newly discovered ultrasonication extraction method provides a fast, easy, and precise way to identify PAHs in airborne particles [81,89,90].

In a study by Wang et al. [91], an ultrasonic extraction method and constant-energy synchronous fluorescence spectroscopy were used to quickly quantify the presence of PAHs in atmospheric particles [91]. Constant-energy synchronous excitation successfully solves the Rayleigh scattering interference of the solution and simplifies the fluorescence emission spectra of PAHs. With a limit of detection and limit of quantification of 0.0580–3.18 and 0.232–12.7 ng·mL⁻¹, respectively, the PAHs were subjected to quantitative measurement at the ideal energy difference. The 15 PAHs had recoveries ranging from 82.8% to 120.0% in the blank and at specific concentrations, and 0.51% to 5.87% for the relative standard deviations [91].

9.5. Soxhlet Extraction

A well-known and often applied technique for extracting PAHs from solid matrices such as soils, sediments, and biological tissues is Soxhlet extraction [35]. This method extracts the target components over a long period of time by continuously washing the solid sample in an appropriate solvent [84]. Dichloromethane, hexane, and toluene are common solvents used in Soxhlet PAH extraction because of their capacity to dissolve non-polar molecules such as PAHs [15]. According to Hawthorne et al. [79], this technique involves placing the solid sample in a thimble and extracting it using a reflux cycle and the proper solvent. The vapour is introduced into the solvent and condenses there before re-dripping onto the solvent in the thimble through a bypass arm as the solvent boils [79]. The process is then repeated until all of the material has been extracted into the bottom flask, at which point the extract and solvent are syphoned back onto it and the solvent boils again [2,79,92].

A Soxhlet extraction could take a few hours to several days, depending on the sample's complexity and the necessary extraction efficiency [15]. The strength, ease of use, and capacity to manage large sample quantities of Soxhlet extraction make it highly regarded. This approach is commonly used because of its high extraction efficiency and repeatability [21]. It does, however, take a long time and much solvent; therefore, handling and disposal must be done carefully to reduce the impact on the environment [8]. Soxhlet extraction yields findings that are comparable to those of other techniques, including ultrasonic, SFE, MAE and ASE techniques. In addition, the results exhibit low relative standard deviations and minor variances [80]. The main drawback of this procedure is the substantial volume of solvent needed; more than 150 mL is required to extract PAHs from a mere 10 g of solid sample [8].

A study by Hawthorne et al. [79] examined the effects of subcritical water extraction, pressurised liquid extraction, Soxhlet extraction, and supercritical fluid extraction on sample matrix, recovery, and selectivity for environmental materials [79]. The various approaches produced some variations in PAH recoveries, but overall, there was strong quantitative agreement across all of the methodologies. The quality of the extract varied significantly, though. The colour of the extracts varied greatly; those from SFE were pale yellow, those from subcritical water were orange, and those from organic solvents (Soxhlet and PLE) were considerably darker [79].

9.6. Accelerated Solvent Extraction

By adding greater pressure, a more recent method called pressured fluid extraction (PFE) or accelerated solvent extraction boosts the solvent's temperature to its boiling point while preserving the liquid phase [26,93]. The high pressure facilitates the solubilisation of air bubbles by increasing the amount of sample exposed to the extraction solvent and improving the heated solvent's capacity to promote solubility [18]. To extract organic compounds from a variety of solid materials, including PAHs, commercial ASE systems are available [85,94]. Once the temperature and pressure have increased appropriately, sediment samples are placed into the extraction cells and an organic solvent is added [85]. It has been observed that the recovery of PAHs from sediments using the ASE technique was double that of Soxhlet extraction. Since high pressures are used, ASE has the advantage of requiring less time overall and less solvent to be used [85]. By employing an online purification column, the extraction process can be totally automated, minimising the loss of volatile PAHs, needless preparation time, and possible contamination that might arise from mechanical shaking [26,95].

A study by Belo et al. [29] optimised an ASE procedure for use with GC-MS for the analysis of eight PAHs in cocoa beans [29]. Relative standard deviations under repeatability and intermediate precision conditions respectively ranged from 2.57 to 14.13% and 4.36 to 19.77%, indicating that the procedure was precise. The eight PAHs had average recoveries ranging from 74.99 to 109.73%. Except for the theoretical limit of detection for chrysene, these parameters, limitations, and measurement uncertainties satisfied the performance standards set by EU legislation [29].

9.7. Solid-Phase Extraction

Solid-phase extraction is a widely used technique for extracting PAHs from environmental samples [78,86]. SPE involves passing a sample through a solid adsorbent material, usually a resin or silica-based sorbent, packed into a cartridge or disc [86]. PAHs are selectively retained based on their chemical properties, such as hydrophobicity and π - π interactions, while the remaining matrix components are washed away. The target analytes become concentrated on the sorbent, as described by Kanchanamayoon and Tatrachun [93]. SPE offers several advantages for PAH extraction from environmental samples, including high selectivity, sensitivity, and reproducibility [86]. It allows for the concentration of analytes from large sample volumes, resulting in lower detection limits [86]. However, SPE also has limitations, such as the need for specialised equipment and consumables, as well

as potential sample loss during the extraction process [78]. Optimisation of SPE parameters, including sorbent selection, solvent choice, and elution conditions, is necessary for the effective extraction of PAHs from environmental samples [78,86].

The study by Ndwabu et al. [33] assessed the levels of PAHs in water samples. To close the knowledge gap about the status of these PAHs in the South African environment, the study evaluated the efficacy of two extraction methods: solid-phase extraction and dispersive liquid-liquid microextraction (DLLME). The techniques' optimisation and validation findings showed that both approaches could be used to extract PAHs from liquid samples. This is because the achieved adequate recovery rates (72.1–118% for SPE and 70.7–88.4% for DLLME) were met. These findings supported the conclusion of the statistical analysis that SPE outperforms DLLME in terms of accuracy and sensitivity [33].

Another study conducted by Ngubo et al. [67] assessed the qualitative and quantitative analysis of PAHs in water and sediment samples using GC-MS after using SPE and ultrasonic extraction procedures [67]. The percentage of PAHs recovered in sediment samples ranged from 82 to 117%, whereas in water samples it ranged from 85 to 121%. The ranges of the limits of quantification and detection for SPE and UE, respectively, were 0.02 to 0.2 µg/L and 0.05 to 0.5 µg/L, and 0.008 to 0.09 and 0.02 to 0.30 µg/kg [67].

9.8. Solid-Phase Microextraction

Solid-phase microextraction is an alternate technique to solvent extraction for extracting PAHs from environmental materials [70]. This solvent-free method puts a fused silica fibre with a tiny diameter that has been covered in an extracting phase into a syringe-shaped device for protection and convenience of handling [78,87,93]. The major advantages of SPME are its speed, simplicity, and convenience, as it can be performed on-site. The SPME device's configuration allows for the extraction of small sample volumes, which can then be analysed without any pre-treatment [21]. To maintain consistency in the qualities and outcomes of the extraction process, however, great accuracy in the manufacturing process is needed to create uniformity in the fibre's construction. Only volatile chemicals, such as LMW PAHs, were found in one investigation that used SPME [87].

Benedetti et al. [7] carried out a study on the validation of an SPME method for solvent-free identification of specific PAHs in plant material used for food supplement preparation. Prioritised PAH detection in bud samples can now be done easily and sustainably with the use of headspace SPME coupled with GC-MS. This approach involves very little sample pre-treatment and very little solvent consumption because it was optimised through response surface techniques and experimental design. For PAHs with masses up to 228 Da, the ultimate technique proved to be precise and sensitive. These analytes achieved reasonable figures of merit with acceptable inter-day precision [7].

9.9. Liquid-Phase Microextraction

PAHs can be extracted from environmental samples with great efficiency and miniaturisation using liquid-phase microextraction (LPME) [25,87]. LPME offers benefits including lower solvent consumption and increased sensitivity by isolating analytes from the sample matrix using a tiny volume of extracting solvent [87]. To obtain the desired results, extraction conditions must be well optimised. Deep eutectic solvents (DESs), ionic liquids (ILs), surfactants, and switchable hydrophilicity solvents are some of the new extraction media for LPME that have been developed recently as a result of performance improvement initiatives [25,94,95]. The primary characteristics of these extraction media include hypotoxicity, low vapour pressure, ease of synthesis and safety. Dispersive liquid-liquid microextraction, hollow-fibre LPME (HF-LPME), and single-drop microextraction (SDME) are the three primary types of LPME methods [87,96,97].

Temerdashev et al. [41] conducted a study on the simultaneous DLLME and analysis of several PAHs in surface water. They proposed a DLLME technique that uses ultrasound assistance and a binary dispersive agent to recover various molecular weight PAHs from water. The centrifugation settings, ultrasonication time, component ratios, and mixture

composition were all taken into consideration when optimising the process for analyte extraction. The analytical methods for removing PAHs from water utilising various extraction and dispersive solvent ratios are presented. When the established sample preparation systems were paired with GC-MS, they were able to identify the analytes at low concentrations (from 0.0002 µg/L) with relative standard deviations of roughly 8% and recoveries reaching 80% [41].

9.10. QuEChERS Method

The QuEChERS method is a popular and effective sample preparation procedure, particularly for the extraction of contaminants such as PAHs from environmental samples [26,45]. The QuEChERS technique was created initially for the measurement of pesticide residue in food, but because of its ease of use and effectiveness, it has been modified for use with a variety of analytes and matrices [26,98–100]. Modifying the extraction solvent, salts, and sorbents employed in the QuEChERS method allows it to be tailored for a variety of environmental sample types. With no need for clean-up procedures or solvent usage, it enables the quick and effective extraction of PAHs [8].

Ostadgholami et al. [101] conducted a study on multivariate optimisation of a modified QuEChERS technique for GC-MS-based PAH detection in grilled meat. After a screening of eleven factors using the Plackett-Burman design, four variables were selected for optimisation with the central composite design (CCD) with the purpose of improving the extraction and clean-up operations of these food contaminants [101]. The GC-MS analysis of a sample produced validated limits of quantitation for PAHs with recoveries ranging from 72–120%. This method minimises matrix effects, improves accuracy, precision, and efficiency, and ensures a control procedure that complies with international standards. Food authorities can use it to identify contaminants of interest in processed meat, thereby preventing food-borne illness and raising public health indices [101].

9.11. Supercritical Fluid Extraction

One sophisticated and effective technique for removing PAHs from environmental samples is supercritical fluid extraction (SFE) [88]. To improve the extraction process, SFE makes use of supercritical fluids, most notably carbon dioxide (CO₂), which possesses characteristics of both liquids and gases. When compared to traditional procedures, SFE enables faster extraction times; it can frequently be completed in less than an hour. High extraction efficiencies are obtained from supercritical CO₂ because it dissolves PAHs and permeates the sample matrix efficiently [80]. It is possible to precisely adjust the extraction parameters (temperature, pressure, co-solvent) to extract PAHs only while minimising the co-extraction of undesirable chemicals [80,88]. Table 4 summarises conventional and modernised extraction methods.

Kariyawasam et al. [2] carried out an investigation on the comparison and optimisation of Eucalyptus Oil-Assisted (EuAE), MAE and SFE of PAHs from sediment and soil samples. The purpose of their study was to compare the extraction efficiency of PAHs from soil and sediment using SFE with ethanol as the modifier, MAE, and EuAE [2]. The EuAE strategy necessitated a longer extraction time than SFE and MAE under ideal conditions, but SFE was the most successful method for removing PAHs from naturally existing soils with variable degrees of contamination [2]. The three techniques yielded similar PAH recoveries, with >80% of applied pyrene, chrysene, and benzo[a]pyrene being recovered [2]. Comparing the environmental impact of extracting PAHs from naturally or intentionally contaminated soils and sediments, ethanol in SFE and eucalyptus oil in EuAE are seen as more environmentally benign than the hexane/acetone employed in MAE [18]. Over 80% of the applied PAHs were recovered using one of the three approaches, with PAH recoveries being comparable [2]. Figure 4 provides a detailed description of the procedures used to extract and quantify PAHs from environmental samples. These procedures include sample collection, sample preparation and extraction, several extraction techniques and final quantification.

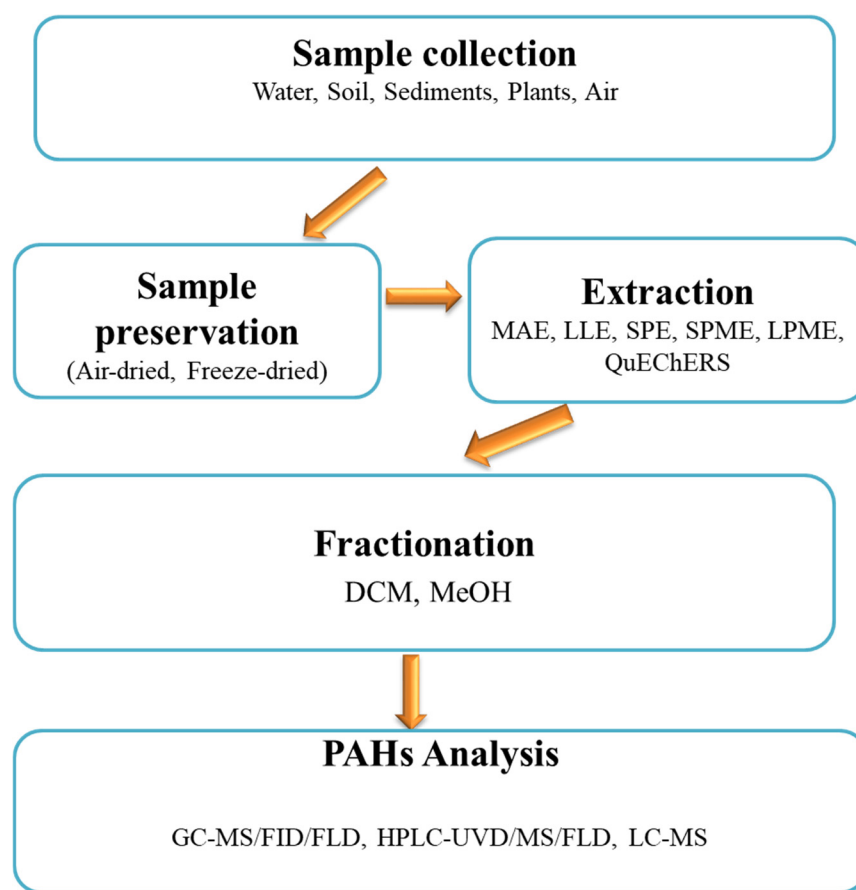


Figure 4. Extraction and quantification procedures of PAHs.

9.12. Magnetic Solid-Phase Extraction

PAHs can be extracted from environmental samples using the novel technology known as magnetic solid-phase extraction (MSPE), which has a number of advantages over conventional techniques [102,103]. With the use of magnetic nanoparticles coated in a selective sorbent, MSPE is able to extract PAHs from complicated matrices quickly, effectively, and with the least amount of solvent [104]. Without the need for centrifugation or filtration, the sorbent can be easily separated from the sample using an external magnet thanks to the magnetic properties of the nanoparticles. This method is very useful for PAH trace analysis since it has great selectivity and sensitivity [104]. Nevertheless, there are certain drawbacks to MSPE, such as the possibility of nanoparticle aggregation, which can lower extraction effectiveness, and the requirement for meticulous condition optimisation to provide reliable results [103,105]. Furthermore, the production and functionalisation of magnetic nanoparticles can be expensive and time-consuming, which might prevent this method from being widely used in everyday environmental investigations [104]. Notwithstanding these obstacles, MSPE is still a viable method for the effective and sustainable extraction of PAHs from a range of environmental materials [103,106,107].

A study by Zhao et al. [105] investigated magnetic solid-phase extraction coupled with HPLC-UV for highly sensitive analysis of monohydroxy PAHs in urine samples. After optimising parameters, the suggested method was able to analyse low-abundance metabolites in huge quantities of complex urine samples with a satisfactory level of sensitivity [105]. Intra-day and inter-day recoveries were 78.0–118.0% and 81.0–115.0%, respectively. The intra-day and inter-day reproducibility were less than 4.5% and 8.6%, respectively. The range for the limits of quantification was 0.030–0.135 ng mL^{−1}, while the range for the limits of detection was 0.009–0.041 ng mL^{−1} [105]. A study by Zhu et al. [108] evaluated magnetic graphene oxide as an adsorbent for the analysis of PAH metabolites in human urine [106].

PAHs had recoveries between 98.3 and 125.2%, relative standard deviations between 6.8 and 15.5%, and limits of detection between 0.01–0.15 ng/mL under ideal circumstances. Human urine monohydroxy PAHs were successfully analysed using this easy, fast, and inexpensive approach [108].

9.13. Gas Purge-Microsyringe Extraction

Gas purge-microsyringe extraction (GP-MSE) is a novel technique for extracting PAHs from environmental samples, offering a unique approach to volatile and semi-volatile compound analysis [105]. The analytes in GP-MSE are extracted from the sample matrix using an inert gas, concentrated in a microsyringe, and then injected straight into an analytical device, like a gas chromatograph [105,106]. This technique has a number of benefits, such as low sample preparation requirements, low solvent consumption, and versatility in handling different kinds of samples, such as liquids, solids, and sludges [104]. Moreover, GP-MSE may provide good recovery rates for PAHs and is quite fast, which makes it appropriate for trace analysis [105–107].

However, GP-MSE also has its drawbacks. To achieve full extraction of target analytes, the approach may need to precisely manage purging conditions, such as temperature and flow rate, which can be difficult to optimise [105]. Additionally, analyte loss during the purging procedure is a possibility, especially for less volatile PAHs, which may compromise the accuracy of the analysis [105,106,109]. Furthermore, the requirement for certain equipment, which not all laboratories have on hand, may limit the method's efficacy [103,105]. Despite these difficulties, GP-MSE is nevertheless a useful method for effectively extracting PAHs, especially in situations where quick analysis and solvent reduction are top concerns [105,110,111].

A study by Zheng et al. [109] assessed GP-MSE for the determination of PAHs in road dust samples [109]. High molecular weight compounds made up between 77.85% and 93.62% of the total mass of PAHs, indicating their substantial dominance. A diagnostic ratio study revealed that the majority of the PAHs found in road dust came from burning coal and biomass combined with petroleum [109]. Using principal component analysis and multiple linear regression, it was shown that the two main sources of road dust particulate matter pollutants (PAHs) were vehicle emissions and biomass/fossil fuel combustions. These sources accounted for 66.7% and 18.8% of the total PAH burden on roads, respectively [109].

The laboratory blank spiked samples had recoveries between 83.7% and 103.5% (RSD b 9.8%), whereas the matrix spiked samples had recoveries between 81.2 and 111.8% (RSD b 14.6%). For every compound, the average relative standard deviations and relative average deviations were 12.3% and 7.9%, respectively [109]. A study by Wang et al. [111] investigated GP-MSE for extracting and determining PAHs from plant samples. The study showed that GP-MSE could offer a quick and thorough way to extract PAHs directly from plant samples [111]. PAHs had recoveries that were almost 100% (83.9–99.4%). The findings showed that PAHs could be fully released from the sample phase in a brief amount of time, and then they could be fully absorbed by the solvent phase [111].

9.14. Sample Preparation and Clean-Up

Preparing and cleaning the sample after PAHs have been extracted from environmental samples is essential to ensure accurate and trustworthy analysis [86]. To eliminate solvents and particle matter from the recovered PAHs, filtration and evaporation are frequently used [11]. While evaporation, which is usually accomplished using rotary evaporators or nitrogen blow-down techniques, concentrates the analytes by eliminating the extraction solvent, filtration aids in the removal of solid contaminants [7,76]. Following these processes, the sample is further cleaned using purification techniques such as column chromatography, which separates PAHs from co-extracted materials that could impede further analysis [8,89]. By efficiently isolating PAHs according to their chemical characteristics, column chromatography, which uses silica gel, alumina, or florisil columns, improves the purity and calibre of the analytes [21]. Reducing matrix effects, enhancing detection

limits, and guaranteeing the accuracy and precision of PAH measurement in environmental samples are all made possible by these cleaning techniques [76].

It is critical to understand that the 16 priority PAHs designated by the EPA are a heterogeneous group with a range of physicochemical characteristics that directly affect the metrological features of analytical techniques, such as accuracy of determination and recovery rates [16]. These variations make it necessary to carefully select extraction methods, analytical techniques, and preparation guidelines that are suited to the particular PAHs under study [62]. Furthermore, careful consideration must be given to the analytical methods chosen, as they may include identifying all 16 priority compounds, a subset of them, or even just one critical pollutant, such as benzo[a]pyrene [18].

Table 4. Comparison of traditional and modernised extraction techniques.

Extraction Technique	Typical Sample Size and Volume	Matrix	Typical Solvent Volume (mL)	Solvent	Duration of Extraction	Advantages	Disadvantages	Reference
Liquid-liquid extraction	200–900 mL	Water	20–200	n-hexane and dichloromethane	3–30 min	Removes PAHs from the sample's suspended particles as well as those that have been adsorbed into the water	Limited selectivity, difficulty of automation and emulsion	[26]
Microwave-assisted extraction	1–10 g	Soil/sediment	10–40	Hexane and acetone	3–30 min	High temperatures, several extractions carried out quickly, little solvent used, and no sample or energy loss	The extraction solvent needs to be microwave-active. Purification of the sample is necessary	[1,2]
Ultrasonication	1–30 g	Soil/sediment	20–200	Acetone, acetonitrile, 2-propanol, cyclohexane, methane and dichloromethane	10–60 min	High efficiency, minimal solvent volumes, and many extractions	Replicas must be used to prove reproducibility. Co-extracted chemicals must be removed	[8]
Solid-phase extraction	1–5 g	Soil/sediment, water	2–20	Methanol, cyclohexane	10–90 min	Quick, selective, low solvent usage, and requires no filtration or clean-up	Sample losses during the elution of impurities from the extract or from irreversible adsorption on solvent material	[102]
Mechanical agitation	1–10 g 100 mL	Soil/sediment, water	1–10	hexane, acetone, dichloromethane	30–120 min	Mechanical agitation can provide efficient extraction of PAHs, particularly when optimised for specific sample types and solvents	Similar to other methods, mechanical agitation may not fully extract highly hydrophobic PAHs from complex matrices without optimisation	[6]
Soxhlet	1–30 g	Soil/sediment	100–600	dichloromethane	3–48 h	Effective extraction with no need for filtration	Clean-up of samples is required. There is extensive usage of solvent volumes	[15]
Accelerated solvent extraction	5–10 g 100 mL	Soil/sediment, water	15–40	hexane, acetone, dichloromethane	15–30 min	ASE significantly reduces extraction time compared to traditional methods	ASE systems can be expensive to purchase and maintain, which may be a barrier for some laboratories	[27]

Table 4. Cont.

Extraction Technique	Typical Sample Size and Volume	Matrix	Typical Solvent Volume (mL)	Solvent	Duration of Extraction	Advantages	Disadvantages	Reference
Solid-phase microextraction	1–5 g	Soil/sediment	Solvent-free	Solvent-free	2–4 h	Fewer steps are required. Least preparation and sample volume	Low selectivity and a finite fibre capacity. Contamination of the SPME needle	[28]
Liquid-phase microextraction	10–100 mL 1–2 g	Soil, sediment, water	0.5–10	hexane, toluene	15–60 min	LPME is economical and ecologically benign because it utilises very little solvent	The small volume of extraction solvent may not be sufficient for highly contaminated samples or for extracting large quantities of analytes	[103]
QuEChERS	1–10 g 10 mL	Soil/sediment, water	1–10	acetonitrile	1–10 min	The method is quick and straightforward, reducing the overall time and complexity of sample preparation	Incomplete extraction of highly hydrophobic PAHs from complex matrices	[26]
Supercritical fluid extraction	5–10 g	Soil, sediment, water	8–50	methanol or acetone	30 min–2 h	SFE offers fast extraction times compared to conventional methods, often completing in less than an hour	SFE systems are expensive to purchase and maintain, which can be a barrier for some laboratories	[42]
Gas purge-microsyringe extraction	1–5 mL	Water	0.1–0.5 mL	n-Hexane	5–15 min	Extremely low solvent usage, rapid extraction	Limited to volatile compounds, requires precise control	[109,111]
Magnetic solid-phase extraction	5–50 mL	Water, soil, sediment	1–5 mL	acetone, methanol	10–30 min	High selectivity, reusability of magnetic materials, fast	Requires magnetic particles, may need additional clean-up steps	[105]

10. Techniques Applied for the Determination of Polycyclic Aromatic Hydrocarbons

10.1. Gas Chromatography

The powerful analytical method known as gas chromatography (GC) is frequently utilised to separate and analyse PAHs in a variety of biological and environmental samples [12,35,112]. Gas chromatography is especially well-suited for analysing the complex combinations of PAHs that are frequently present in contaminated samples because of its high sensitivity and resolution [89]. When it comes to PAH analysis, GC is incredibly sensitive, accurate, and capable of finding PAHs at low amounts [78,113,114]. It is widely used in food safety, health risk assessments, and environmental monitoring to make sure that regulations are followed and to comprehend the distribution and effects of PAHs in the environment [115,116]. To guarantee accurate and repeatable results, routine GC system maintenance, method validation, and calibration are crucial [35].

Gas chromatography is an invaluable technique for examining liquid and gaseous samples that contain hundreds of distinct compounds [88]. It enables analysts to determine the kinds of molecular species that are present as well as their quantities [89]. According to Soursou et al. [51], the process involves injecting a sample mixture into a mobile phase that interacts with a stationary phase, causing the components to separate based on their rate of contact [51]. For use in additional analysis, the resultant chromatogram offers details on the PAH compounds' sequence of elution. As the device operates, the computer uses the

signal to form a graph known as a chromatogram, where each peak denotes the signal that is produced when a PAH chemical leaves the GC column and enters the detector [91,113].

Selecting the correct detector for gas chromatography analysis of PAHs is essential for producing sensitive and reliable results [91]. The Flame Ionisation Detector (FID) and the Mass Spectrometer (MS) are two frequently used detectors for PAH analysis [89]. Because of its exceptional sensitivity and efficiency, the mass spectrometer is the most widely used detector [89,111]. It has the benefit of offering data on PAHs that is both quantitative and qualitative. FID and MS both have unique benefits [1]. Since FID is simple to use and reasonably priced, it is a highly effective method for routinely quantifying PAHs. On the other hand, MS offers more sensitive and precise molecular information, which is necessary for recognising and quantifying low quantities of PAHs in complicated samples. Either or both detectors can be used, depending on the analytical needs, to guarantee thorough and precise PAH analysis utilising gas chromatography [35,49].

The Fluorescence Detector (FLD) is another popular detector type in gas chromatography that is utilised for the quantification of PAHs [23,112]. Fluorescence emission serves as the foundation for FLD's operation because PAHs are naturally fluorescent substances, producing light at longer wavelengths and absorbing light at particular wavelengths. Following their elution from the GC column, PAH molecules travel through a cell that is exposed to ultraviolet (UV) radiation [79,113]. The PAH molecules are excited by this UV radiation, which makes them glow. Next, the released fluorescence is found and measured [31]. Because of its high sensitivity, selectivity, and capacity to yield both qualitative and quantitative information on PAH chemicals in complicated environments, GC-FLD is an effective analytical approach for the quantification of PAHs in environmental samples [1,114,115].

A study on PAH analysis using magnetic three-dimensional graphene solid-phase extraction coupled with GC-MS was carried out by Sereshti et al. [117]. They developed a composite material in their study that included iron oxide nanoparticles and three-dimensional graphene aerogel [117]. This material was then used to extract PAH compounds using magnetic solid-phase extraction using gas chromatography-mass spectrometry/selected ion monitoring (GC-MS/SIM) analysis. The relative standard deviations (RSD) for the intra- and inter-day precisions were determined to be 3.9% and 4.7%, respectively. The suggested technique was effectively used to identify PAHs in tap, river, and rainwater samples; recoveries between 71 and 110% were attained [117].

A new 10 m short GC column in conjunction with a GC/MS was evaluated by Zhang et al. [118] to identify 16 PAHs in soil, with five deuterium internal standards and two replacements [103]. The total analysis of these samples took 10 min because the chromatograph column was short. Although the response is quicker, the rapid chromatogram and the standard technique are similar. PAHs had an excellent linear relationship on the rapid column in the range of 5.0–400 $\mu\text{g}\cdot\text{L}^{-1}$, with a correlation coefficient $R > 0.997$ and a LOD of 0.04–0.38 $\mu\text{g}\cdot\text{kg}^{-1}$. This approach reduces costs while simultaneously increasing detection efficiency [118].

A study on the simultaneous assessment of PAHs in groundwater by GC-FID following solid-phase extraction was carried out by Carvalho et al. [47]. Their study's aim was to evaluate and ascertain the amounts of PAHs in groundwater samples taken from tube wells in a northern Brazilian city using GC-FID [47]. Solid-phase extraction cartridges were used to pre-treat samples in order to enhance the PAH fraction of interest and remove interferences from the matrix, which improved PAH identification in samples using GC-FID. Using the addition and recovery approach, the recoveries for PAHs varied from 85.4 to 105.7% with good precision ($\text{RSD} < 5.0\%$). The study's findings demonstrated that the technique for analysing PAHs in groundwater samples is quick, precise, reliable, and highly efficient [47]. Table 5 presents a comparative summary of the quantities of PAHs in diverse environmental samples, emphasising the range of study locations, sample types, extraction strategies, and analysis methodologies.

Table 5. Comparison of total concentrations of PAHs reported from different places in the world.

Location	Type of Sample	No. of PAHs	Percentage Recovery	Extraction Method	Analysis Technique	PAHs Concentrations Range	Reference
Tehran (northern Iran)	Water	13	71–110%	SPE	GC-MS	0–43.45 ng mL ^{−1}	[117]
Yanco, New South Wales (NSW), Australia	Soil & sediment	4	32.6–116.7%	SFE, MAE, eucalyptus oil-assisted extraction	GC-MS	4–3500 µg/kg	[2]
Polokwane, South Africa	Water	16	67.6–115%	LLE	GC-FID	0.0121–1.53 µg/L	[26]
Vietnam	Tea leaves	4	98–112%	QuEChERS	HPLC-FLD	2.88–218.21 µg/kg	[100]
Norway	Water	16	57–104%	ASE, SPE	HPLC-DAD-FLD	0.020–2.0 µg/g	[116]
Spain	Toasted cereals	15	70.1–109%	MAE	HPLC-UV-FLD	Not detected	[119]
Karasun Lake, Azov Sea, Black Sea, Russia	Lake Water, Sea Water, Tap Water (Krasnodar)	20	74–111%	DLLME	GC-MS, HPLC-FD/PDA	0.1–20 ng/L	[41]
Polokwane, South Africa	Sediment	16	23.1–125%	MAE, ultrasonication, mechanical shaking	GC-FID	0.016–10.8 mg/kg	[8]
North Dakota, United States	Soil	17	–	Soxhlet, pressurised liquid extraction, SFE	GC-FID	2–502 mg/kg	[79]
Turin, Italy	Plants	16	88–105%	SPME	GC-MS	3.4–42 ng/g	[7]

10.2. High-Performance Liquid Chromatography

Another popular technique for analysing PAHs is high-performance liquid chromatography, especially for less volatile or thermally labile PAHs [35,120]. Numerous detectors, including UV-Vis, fluorescence, and mass spectrometry, can be used for detection [82,121]. These techniques are very sensitive and highly automated. The ability to use extremely sensitive and selective detectors is one of the main benefits of determining PAH using HPLC [93]. It is well known that aromatic compound molecules may absorb UV light, and some PAHs have strong fluorescence. Liquid chromatography analysis of PAH has been commonly used for detectors operating according to the aforementioned principles [82]. Many solvents show only a slight absorption at the wavelength used in the detection [121]. Both ultraviolet detection (UVD) and fluorometric detection are used in HPLC for the study of PAHs [120].

Woźniak et al. [78] carried out a study on the use of HPLC to determine the PAH content of garden herbal plants. This study's goal was to ascertain whether PAHs have contaminated three common herbal species: mint, parsley, and lavender [78]. The plants came from three different Polish backyard gardens. Eleven PAHs were quantified using high-pressure liquid chromatography in plant material that had been isolated using the QuEChERS purification technique. The data obtained indicated that the species and cultivation site of herbs affect the degree and kind of PAH contamination in plants. Particularly in facilities related to the mining and energy sectors, PAHs can contaminate plant material meant for direct use or use in bioactive herbal extracts [78].

Moreover, Wang et al. [121] constructed an online system utilising HPLC to analyse the substances under test [121]. Under ideal circumstances, the online analysis method yielded good linearity (0.03–30 µg·L^{−1}), low detection limits (0.01–0.10 µg·L^{−1}), and high enrichment factors (77.6–678). This approach was used to identify target analytes in coal,

ash and river water samples, with recoveries falling into the range of 80.6–106.6 and 80.9–103.5%, respectively [121].

10.3. Supercritical Fluid Chromatography

Supercritical fluid chromatography (SFC) is an additional widely used technique for PAH analysis [88,122]. SFC is used to measure HMW and low quantities of organic chemicals such as PAHs. It is typically employed in the examination of medicinal drugs, petroleum, polymers, and propellants [80]. Similar to GC and LC, SFC uses liquid carbon dioxide as the mobile phase, which results in a highly pressurised flow path [80]. Furthermore, because of the low viscosity and strong eluting power of carbon dioxide, SFC separations for the identification of PAHs are frequently faster than those achieved by liquid solvents [88,122]. Initially, pure carbon dioxide (CO₂) was used as the mobile phase in supercritical fluid chromatography. However, since an organic addition or modifier to increase the solubility of polar molecules can alter CO₂, SFC is now frequently performed in subcritical conditions. The high molecular diffusiveness and low viscosity are associated with these characteristics [75,95]. Higher flow rates and smaller pressure fluctuations across the column can be employed using SFC, as opposed to HPLC, for shorter analysis periods and less organic solvent consumption [88].

Zhang et al. [122] used supercritical fluid chromatography-mass spectrometry to analyse parent and oxygenated PAHs in milk. Their research developed a rapid and precise SFC-MS technique to detect PAHs in three different types of liquid milks: ten ultra-heat treated (UHT) milks, eight pasteurised milks, and four pasteurised milks with an extended shelf life [122]. The instrumental analysis took 15 min, yielding a recovery of 67.66–118.46%. The findings imply that in order to estimate future risks, impose restrictions, and provide dietary recommendations, raw milks should be closely monitored and thoroughly tested for PAH concentrations [122].

Lübeck et al. [123] carried out a study on the use of SFC for the identification of oxygenated PAHs in unconventional oils. They combined the investigation of PAHs and oxygenated polycyclic aromatic compounds (OPACs) using SFC [123]. Chromatographic separation of PAHs from OPACs was one goal; achieving high peak capacity, enhanced peak morphologies, and high signal-to-noise ratios (S/N) for OPACs was another. The objective was to create a non-target analytical method for oxygenated compounds in unconventional oils by utilising SFC hyphenated to a UV detector and a quadrupole time-of-flight mass spectrometer (QTOF-MS) with negative electrospray ionisation. The best method for separating PAHs from OPACs was discovered to be the silica column with an ethylene bridge. Utilising a pyrolysis oil and a coal tar middle distillate, the optimised SFC-UV-ESI-QTOF-MS method was assessed [123].

10.4. Capillary Electrophoresis and Thin-Layer Chromatography

Capillary electrophoresis (CE) is another often-used method for identifying PAHs in environmental samples [48,124,125]. For the investigation of PAHs, CE can be combined with a variety of detection techniques, such as fluorescence and UV-Vis. Thin-Layer Chromatography (TLC) is an easy and affordable method to separate PAHs [97]. It entails the separation of PAHs on a thin layer of an absorbent substance, which is followed by chemical staining or UV light visualisation [98]. A thorough comparison of the analytical techniques for identifying PAHs in environmental samples is presented in Table 6, with an emphasis on the methods' benefits, drawbacks, turnaround times, and suitability for different sample matrices.

In a study conducted by Chen et al. [126], capillary electrophoresis was used to identify different PAH types, including benzantracene and fluoranthene [126]. The measured substance could be quickly identified in 27 min after the ideal experimental conditions were established, including the concentration of surfactant, the makeup of the microemulsion, and the duration of the high conductivity buffer. This technique was applied to the

identification of brand cosmetics, and the recovery rate ranged from 90.6% to 95.9%, with a relative standard deviation of 3.3% to 5.1% [126].

Table 6. Comparison of various analytical techniques for determining PAHs in environmental samples.

Analytical Technique	Advantages	Limitations	Time Required	Sample Matrix	Operating Conditions	Selectivity for Size	References
Gas Chromatography-Mass Spectrometry	- Identifies and quantifies multiple PAHs - Widely used	- Requires extensive sample preparation - High cost of equipment and maintenance - Time-consuming analysis	- Sample prep: Hours - Analysis: 30–60 min/sample	- Air, water, soil, sediments	- Requires high-purity gases- - Operates at high temperatures (200–300 °C)	- High selectivity for PAHs based on volatility and molecular size	[9,35,64,112]
High-Performance Liquid Chromatography	- Effective for higher molecular weight PAHs - Good separation efficiency - Less sample prep than GC-MS	- Lower sensitivity than GC-MS - Requires fluorescence or UV detection for PAHs - Can be costly	- Sample prep: Hours - Analysis: 20–30 min/sample	- Water, soil, sediments	- Operates at room to moderate temperatures (20–40 °C)	- Can be tailored with different column phases for size selectivity	[34,78,100,105]
Fluorescence Spectroscopy	- High sensitivity for specific PAHs - Rapid analysis - Relatively low cost	- Limited to fluorescent PAHs - Requires calibration with standards - Potential for matrix interference	- Sample prep: Minimal - Analysis: Minutes/sample	- Water, soil	- Operates under ambient conditions with UV/Vis light	- Selective for PAHs with specific ring sizes that fluoresce	[127,128]
Fourier Transform Infrared Spectroscopy (FTIR)	- Non-destructive - Rapid analysis - Minimal sample preparation	- Limited sensitivity for trace levels - Interference from other compounds	- Sample prep: Minimal - Analysis: Minutes/sample	- Water, soil, sediments, air	- Operates at room temperature with IR light	- Limited selectivity; depends on molecular vibration modes	[129,130]
Gas Chromatography with Flame Ionisation Detection	- Good sensitivity and specificity - Lower cost than GC-MS - Reliable and robust	- Lower sensitivity than GC-MS - Cannot identify PAHs without standards - Requires sample clean-up	- Sample prep: Hours - Analysis: 30–60 min/sample	- Air, water, soil, sediments	- Requires high purity gases- - Operates at high temperatures (200–300 °C)	- High selectivity for PAHs based on volatility and molecular size	[8,26]
Surface-Enhanced Raman Spectroscopy (SERS)	- High sensitivity and specificity - Minimal sample preparation - Rapid detection	- Requires specialised substrates - Potential variability in substrate performance	- Sample prep: Minimal - Analysis: Minutes/sample	- Water, soil	- Operates at room temperature with laser excitation	- Limited selectivity; depends on molecule-surface interactions	[131]

Table 6. Cont.

Analytical Technique	Advantages	Limitations	Time Required	Sample Matrix	Operating Conditions	Selectivity for Size	References
Electrochemical Methods	- Simple and portable - Rapid and on-site analysis - Low cost	- Lower sensitivity and selectivity compared to chromatographic methods - Requires calibration	- Sample prep: Minimal - Analysis: Minutes/sample	- Water, soil	- Operates at ambient temperature with applied voltage	- Selectivity can be tuned with specific electrodes or coatings	[51]
Supercritical Fluid Chromatography	- Fast separation - Lower solvent consumption - High resolution for non-polar compounds	- Requires specialised equipment - Limited availability - Expertise needed for method development	- Sample prep: Hours - Analysis: 10–30 min/sample	- Water, soil, sediments	- Operates with supercritical CO₂ at high pressure	- Selective based on molecular weight and polarity	[104]
Capillary Electrophoresis	- High separation efficiency - Minimal sample volume required - Rapid analysis	- Limited to charged or polar PAHs - Lower sensitivity compared to chromatographic methods - Complex data interpretation	- Sample prep: Hours - Analysis: Minutes/sample	- Water, soil, sediments	- Operates at high voltage-Requires precise pH control	- Selectivity based on charge-to-size ratio	[122]
Thin-Layer Chromatography	- Simple and inexpensive - Visual detection possible - Rapid screening tool	- Low sensitivity and resolution - Semi-quantitative at best - Requires further analysis for confirmation	- Sample prep: Minimal - Analysis: Minutes/sample	- Water, soil, sediments, air	- Operates at ambient temperature-Requires solvent	- Limited selectivity; separates based on polarity and size	[124]
Synchronous Fluorescence Spectrophotometry	- High sensitivity and selectivity - Reduces spectral overlap - Rapid analysis	- Limited to PAHs that fluoresce - Requires specific instruments	- Sample prep: Minimal - Analysis: Minutes/sample	- Water, soil	- Controlled wavelength settings, typically room temperature	- High, sensitive to specific PAHs due to fluorescence properties	[132]
Near-Infrared (NIR) Spectroscopy	- Non-destructive - Rapid and simple sample preparation	- Lower sensitivity for PAHs - Requires calibration with standards	- Sample prep: Minimal - Analysis: Minutes/sample	- Water, soil, sediments	- Requires controlled light source and detector	- Low, better for bulk characterisation	[133]
Miniaturised Membrane Inlet Mass Spectrometer (mini-MIMS)	- High sensitivity and specificity - Portable and allows on-site analysis	- High initial cost - Requires technical expertise	- Sample prep: Minimal - Analysis: Minutes/sample	- Water, soil	- Operates under vacuum and controlled temperature	- Moderate, depending on membrane selectivity	[83]

Table 6. Cont.

Analytical Technique	Advantages	Limitations	Time Required	Sample Matrix	Operating Conditions	Selectivity for Size	References
Polythiophene Sensors	- High sensitivity - Can be used for real-time monitoring - Low cost	- Limited to specific PAHs - Potential for sensor fouling	- Sample prep: Minimal - Analysis: Minutes/sample	- Water, air	- Ambient conditions	- High for certain PAHs due to functionalisation	[134]
Graphene Nanosensor	- High sensitivity and selectivity - Fast response time - Potential for real-time monitoring	- High development cost - Requires calibration and potential for fouling	- Sample prep: Minimal - Analysis: Minutes/sample	- Water, soil, air	- Ambient conditions	- High, tunable based on functionalisation	[135]
Liquid Chromatography-Mass Spectrometry	- Capable of identifying and quantifying multiple PAHs simultaneously	- High cost of equipment and maintenance - Requires extensive sample preparation	- Sample prep: Hours - Analysis: 30–60 min/sample	- Water, soil, sediments, air	- Requires precise temperature and pressure control	- Moderate, depending on column and ionisation source	[37]

11. Application of Hybrid Techniques

In recent times, hybrid techniques such as HPLC-MS and gas chromatography-tandem mass spectrometry (GC-MS/MS) have become essential for the extraction and identification of PAHs from environmental samples [6,81]. These cutting-edge analytical techniques enable the accurate identification and quantification of PAHs, even in complex matrices, by combining the strong detection capabilities of mass spectrometry with the high separation efficiency of chromatography [79]. Particularly, GC-MS/MS provides improved sensitivity and specificity, making it possible to distinguish between isomeric molecules and to detect low amounts of PAHs [118]. In a similar vein, HPLC-MS offers solid and trustworthy results, particularly when analysing less volatile and thermally labile PAHs [6,21,136]. By using these hybrid techniques, PAH analysis can be performed with much more precision, sensitivity, and repeatability, leading to a better knowledge of the distribution, origins, and environmental impact of PAHs [79].

These hybrid methods make it possible to precisely separate and identify PAHs in complex matrices such as soil, water, and air, even at trace levels [119–121]. Since LC-MS can handle non-volatile and thermally labile chemicals, it is preferable for detecting higher molecular weight PAHs [61]. Published research has shown that GC-MS is useful in detecting lower molecular weight PAHs [61,119,122]. Chromatographs from recent publications demonstrate the distinct separation of PAH peaks, highlighting the resilience of these hybrid methods in offering thorough environmental evaluations [7,12,61]. The synergistic effects of these hybrid techniques have also been highlighted in these studies. Specifically, in samples with low concentrations or complex mixtures, the combination of mass spectrometric detection and chromatographic separation improves the accuracy and reliability of PAH identification [98]. These developments highlight the vital role hybrid approaches play in environmental monitoring as well as the continuous development of increasingly complex analytical techniques for PAH identification [61,123,124].

A study by Sulej-Suchomska et al. [137] developed a dependable and accurate analytical method for the simultaneous determination of 16 PAHs in different types of airport runoff water [137]. They used SPME combined with comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GCGC/TOF-MS) for PAH analysis [137]. This approach yielded a recovery of 63–108%, most of which was within the allowable range for the analytical processes. Furthermore, the devised process demon-

strated acceptable accuracy, selectivity, and low limit of detection values, which were $2.20 \text{ ng}\cdot\text{L}^{-1}$ for phenanthrene and $0.22 \text{ ng}\cdot\text{L}^{-1}$ for benzo[k]fluoranthene, respectively. This approach can be used to monitor the fate of PAHs in the ecosystem and evaluate the effects of airports on the environment [137].

12. Challenges and Limitations

There are many analytical difficulties in removing and identifying PAHs from environmental samples, especially when working with complex matrices such as soil, sediments, and biota [7,125,126]. The presence of numerous interfering compounds in these matrices might cause PAHs to co-extract, making the process of separating and quantifying them more difficult [11,127,128]. For example, organic matter, humic compounds, and other contaminants, which could result in analytical errors, may obscure the target PAHs [68]. In order to ensure that the PAHs can be precisely recognised and quantified among the numerous other compounds present in the samples, it is necessary to create strong clean-up procedures and highly selective extraction methods [87,129].

The present extraction and identification techniques for PAHs still have some significant drawbacks [2,130]. Numerous conventional methods, such as LLE and Soxhlet extraction, are labour- and time-intensive and frequently call for huge amounts of dangerous solvents [2,11]. Even while more recent techniques such as MAE and SPE provide advances, issues such as matrix effects and insufficient PAH recovery might still be a challenge. Additional difficulties are presented by the variety of environmental sample types and the fluctuations in PAH concentrations [98,132,133]. To guarantee uniformity and dependability across various investigations and labs, these procedures urgently need to be standardised and validated. Standardised procedures would make it easier to compare results, boost the quality of the data, and advance our knowledge of the distribution and effects of PAHs in the environment [14].

13. Future Directions and Emerging Trends

Green chemistry, which attempts to lessen the environmental impact of chemical operations, is having a growing impact on PAH analysis [68,104]. In this context, the development of solvent-reducing or solvent-free extraction techniques such as MAE and SFE is becoming more and more important [2,134,135]. These techniques are more sustainable since they not only use fewer dangerous solvents but also frequently need less time and energy. In line with the goals of green chemistry, researchers are also looking into the use of less toxic and biodegradable solvents for SPE and LLE [70]. Not only can the application of green chemistry concepts to PAH analysis increase environmental sustainability, but it also makes analytical techniques safer and more economical [104].

In addition to these developments, the field is seeing notable breakthroughs in automation and miniaturisation, as well as in extraction and detection technologies [61]. On-site analysis is now possible because of the development of portable and compact analytical instruments such as lab-on-a-chip systems and microextraction techniques, which eliminate the need for substantial sample storage and transit [97]. Automation is also becoming more common in sample preparation and analysis, which reduces human error while increasing throughput and reproducibility [16,136]. More sensitivity and specificity are provided by advanced detection technologies, such as improved mass spectrometry and two-dimensional gas chromatography (GC/GC), which make it possible to find trace amounts of PAHs in intricate matrices [61]. By increasing the effectiveness, accuracy, and accessibility of PAH analysis, these new developments have the potential to completely transform the field and improve environmental monitoring and protection in the process [16,137].

14. Conclusions

This review has provided a comprehensive outline of recent advancements in the identification and extraction of PAHs from environmental samples. Through the examination

of various analytical techniques, extraction methods, and advancements in instrumentation, researchers have made significant strides in improving the sensitivity, accuracy, and efficiency of PAH analysis. The development of novel extraction techniques, such as MAE, SPME and LPME, offers promising avenues for enhancing the detection of PAHs in complex environmental matrices. Furthermore, the integration of emerging technologies, such as mass spectrometry and chromatography, has facilitated the identification of PAHs at trace levels, enabling a deeper understanding of their distribution and environmental impact. However, challenges remain, particularly in addressing the diversity of PAH compounds and the complexity of environmental matrices. Future research efforts should focus on refining existing methods, exploring innovative approaches, and establishing standardised protocols to ensure reliable and reproducible analysis of PAHs in environmental samples. By continuing to advance our understanding of PAH identification and extraction, we can better assess environmental contamination, mitigate associated risks to human health, and develop effective strategies for pollution prevention and remediation. By staying informed of the latest developments and technologies, researchers can continue to make strides in the field of environmental monitoring and protection.

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