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Polycyclic Aromatic Hydrocarbons (PAHs) in inland aquatic ecosystems: Perils and remedies through biosensors and bioremediation☆

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ABSTRACT

Polycyclic **A**romatic **H**ydrocarbons (**PAHs**) are among the most ubiquitous environmental pollutants of high global concern. PAHs belong to a diverse family of hydrocarbons with over one hundred compounds known, each containing at least two aromatic rings in their structure. Due to hydrophobic nature, PAHs tend to accumulate in the aquatic sediments, leading to bioaccumulation and elevated concentrations over time. In addition to their well-manifested mutagenic and carcinogenic effects in humans, they pose severe detrimental effects to aquatic life. The high eco-toxicity of PAHs has attracted a number of reviews, each dealing specifically with individual aspects of this global pollutant. However, efficient management of PAHs warrants a holistic approach that combines a thorough understanding of their physico-chemical properties, modes of environmental distribution and bioaccumulation, efficient detection, and bioremediation strategies. Currently, there is a lack of a comprehensive study that amalgamates all these aspects together. The current review, for the first time, overcomes this constraint, through providing a high level comprehensive understanding of the complexities faced during PAH management, while also recommending future directions through potentially viable solutions. Importantly, effective management of PAHs strongly relies upon reliable detection tools, which are currently non-existent, or at the very best inefficient, and therefore have a strong prospect of future development. Notably, the currently available biosensor technologies for PAH monitoring have not so far been compiled together, and therefore a significant focus of this article is on biosensor technologies that are critical for timely detection and efficient management of PAHs. This review is focussed on inland aquatic ecosystems with an emphasis on fish biodiversity, as fish remains a major source of food and livelihood for a large proportion of the global population. This thought provoking study is likely to instigate new collaborative approaches for protecting aquatic biodiversity from PAHs-induced eco-toxicity.

1. Introduction

Sustainability is not an option – it is a matter of how it is achieved. Degradation of the world's natural resources is rapidly outpacing the planet's ability to absorb the damage. This is primarily due to the extensive anthropogenic activities that along with unavoidable natural events have led to the deposition of a wide range of toxic compounds in the environment, turning this issue into an alarming global concern (Gianfreda and Rao, 2008). Today, one of

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the major environmental concerns in urban and industrial areas is **P**olycyclic **A**romatic **H**ydrocarbons (**PAHs**) as they pose a major threat towards global pollution. PAHs belong to the class of persistent organic hydrocarbons that consist of two or more fused aromatic rings (Fetzer, 2000; Igwe and Ukaogo, 2015; Sims and Overcash, 1983). One of the critical concerns with PAHs is their omnipresence in air, water, soil and aquatic sediments and high dwell time in the environment (Mrozik et al., 2003). Due to their high hydrophobicity, PAHs are difficult to be washed-off, and particularly in aquatic environments, they tend to get adsorbed on particulate matters and remain adsorbed for long periods. Among the hydrocarbon family of organic molecules, PAHs remain the most widely distributed toxic (Bamforth and Singleton, 2005; Samanta et al., 2002; Zhu et al., 2009), causing a number of adverse effects to aquatic organisms, including endocrine alteration (Meador et al., 2006), growth reduction (Christiansen and George, 1995), DNA damage (Caliani et al., 2009) and malformations of embryos and larvae (Carls et al., 2008). Fishes offer a good indicator of PAH pollution in water bodies (Nyarko and Klubi, 2011), as due to the high stability and lipophilicity of PAH (Bouloubassi et al., 2001), these get accumulated in fatty tissues of fish (Van der Oost et al., 1991) when ingested either through food (Meador et al., 1995) or through sorption *via* skin and gills (Gobas et al., 1999).

Fishes have been recognized as an important source of human protein diet, providing ~17% of the global intake of animal protein and 6.7% of all proteins (FAO, 2016). A large section of the human population depends on fisheries to meet their livelihood and nutritional requirements. However, with a significant increase in the anthropogenic activity in recent years, along with unavoidable process of biotransformation and biomagnification, the levels of PAH-based pollutants have become alarmingly high in the aquatic ecosystem (Nwaichi and Ntorgbo, 2016). The eventual consumption of these contaminated fishes has become an important pathway for human exposure to PAHs. Overall, thousands of PAHs are present in the environment but most of the studies remain focused on 16 priority pollutants (Yan et al., 2004) including potential human carcinogen, such as benzo[*a*]pyrene, chrysene, and benzo[*a*] anthracene (Andersson and Achten, 2015; Yan et al., 2004). For efficient environmental management of PAHs, it is important to co-consider multiple aspects in parallel, including their (i) distribution and eco-toxic effects, (ii) detection strategies, and (iii) potential remediation pathways. Considering the importance of PAHs, over the past decade, a number of reviews have been written on topics related to PAHs. The first category of reviews has focused on sources of PAHs in environments, their fate, and ecotoxic effects (Hamid et al., 2016; Hylland, 2006; Lawal, 2017; Meador et al., 1995). Another series of reviews has focused on potential remediation strategies for PAH-contaminated sites (Abdel-Shafy and Mansour, 2016; Haritash and Kaushik, 2009; Wilson and Jones, 1993). On the other hand, the current and potentially new detection strategies to identify PAHs have not yet been reviewed. Importantly, a review that consolidates all these PAH-related interdependent topics thereby providing a comprehensive understanding remains unavailable. Since the aquatic environment is the most critical contributor to the toxicity of PAHs, the current review focuses on critically analyzing the physico-chemical properties of PAHs, their source and distribution in aquifers, effect on aquatic organisms, existing approaches for their detection, and potential remediation strategies by employing catabolically diverse microbial community.

2. Physico-chemical properties of PAHs

The general characteristics of PAHs include high melting and boiling points, low vapor pressure, and poor water solubility (WHO, 1998). Individual PAHs vary in volatility and water solubility. The low molecular weight PAHs (two or three rings) are more easily degradable than those with higher molecular weights (four or more rings) due to relatively higher volatility and solubility of the former. Besides, the high molecular weight PAHs have the property to remain strongly fixated to soil sediments, thereby becoming resistant to microbial degradation. The incombustible nature of PAHs further keeps them persistent in the environment for long periods of time. PAHs are pollutants of high concern due to their toxic and growth/sex modulation effects not only towards aquatic organisms, but also in higher order animals and humans through bioaccumulation, leading to mutagenicity, carcinogenicity and genotoxicity (EC, 2002). The chemical structures of environmentally important PAHs are provided in Fig. 1 and their physico-chemical characteristics are enlisted in Table 1.

3. Environmental distribution of PAHs

3.1. Sources of PAHs in non-aquatic ecosystems

The last century of industrial development has caused a significant increase in PAHs concentrations in the environment (Wild and Jones, 1995). Three major sources of PAHs in the environments are pyrogenic, petrogenic and phytogenic (Fig. 2). In a pyrogenic process, PAHs are formed during pyrolysis where organic substances are burned at high temperatures ($\geq$350 °C) under low oxygen or anaerobic conditions. PAHs from pyrogenic activities are mostly found in urban areas (Abdel-Shafy and Mansour, 2016). Some of the largest sources of pyrogenic PAHs include the production of coke and coal tar during destructive distillation of coal, and the thermal conversion of crude petroleum into lighter hydrocarbon fractions (Enzminger and Ahlert, 1987; Guerin et al., 1977). Pyrogenic PAHs are also unintentionally formed during incomplete combustion of fuel in motor vehicles and power generators, and the woods during forest fires (Zou et al., 2003). In contrast, petrogenic PAHs are formed naturally during crude oil maturation over millions of years at low temperature (100–150 °C) (Abdel-Shafy and Mansour, 2016). These petrogenic PAHs get disseminated in the environment anthropogenically during transport, storage and use of crude oil and crude oil products (Stogiannidis and Laane, 2015). The major source of petrogenic PAHs in the ocean and fresh water are due to oil spills and storage tank leaks (Stogiannidis and Laane, 2015). Phytogenic (or more broadly biogenic) sources of PAHs include synthesis of such molecules by plants and lower order organisms such as bacteria and algae (Krauss et al., 2005). For instance, naphthalene, phenanthrene and their derivatives in plant wood of the Amazon basins were found to be accumulated in the termite nests (Wilcke et al., 2000). In fact, naphthalene concentrations in the plants and termite nests of tropical rainforest of Brazil were found to be as high as 1000 $\mu g\, kg^{-1}$ and 160 $\mu g\, kg^{-1}$, respectively (Krauss et al., 2005).

According to the World Health Organization, the smoke produced from combustion processes, such as in motor vehicles, from open fire places and tobacco consumption contains significant amounts of PAHs (WHO, 2010). It was estimated that worldwide 530,000 tons of 16 priority PAHs were emitted in the year 2004 alone, with China leading with 114,000 tons, followed by India with 90,000 tons, and the United States of America with 32,000 tons (Zhang and Tao, 2009). In coal processing plants, coal tar pitch is produced as a waste product. This coal tar loaded with hundreds of PAHs is widely used in road surfaces as a binding agent. Though in some developed countries, the awareness towards PAHs has led to the restricted use of tar; in many developing nations, it is still widely used in a number of products; for instance, for making water-proof roofs (Trumbore et al., 2015). High contents of PAHs have also been detected in consumer goods, such as in bicycles,

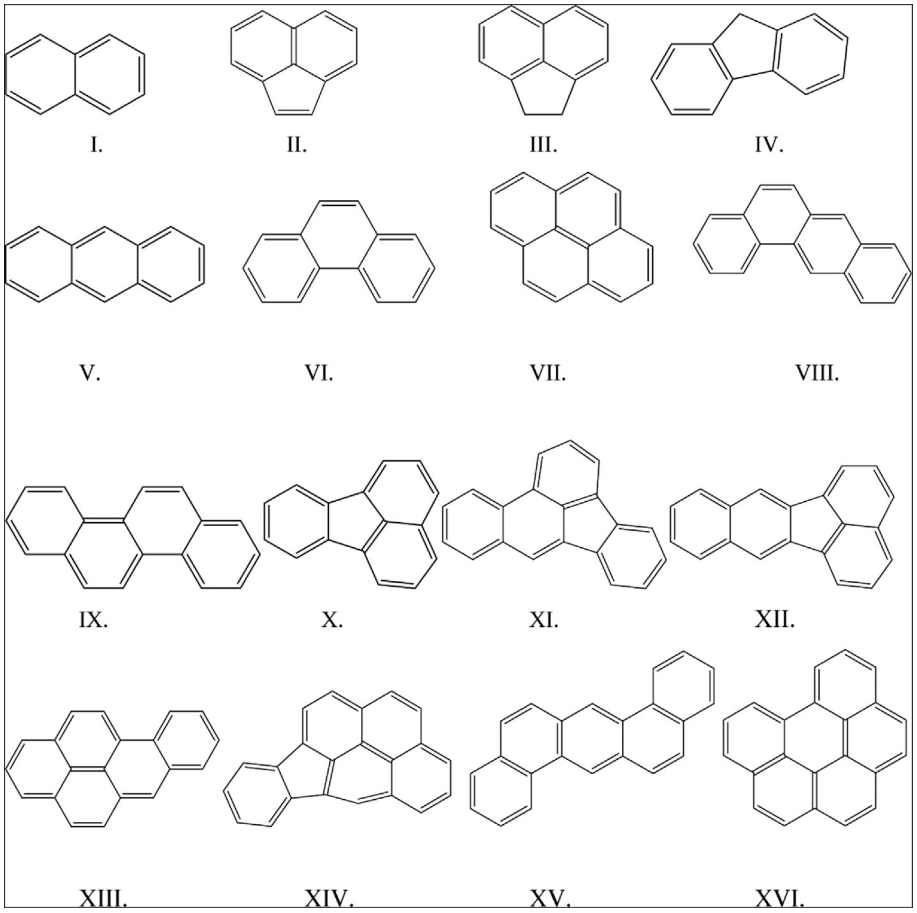

Fig. 1. Chemical structures of US EPA listed priority PAHs. (I) naphthalene (II); acenaphthylene; (III) acenaphthene; (IV) fluorene; (V) anthracene; (VI) phenanthrene; (VII) pyrene; (VIII) benzo[*a*]anthracene; (IX) chrysene; (X) fluranthene; (XI) benzo[*b*] fluoranthene; (XII) benzo[*k*]fluoranthene; (XIII) benzo[*a*]pyrene; (XIV) indeno[*1,2,3-c,d*]pyrene; (XV) fibenzo [*a,h*]anthracene; and (XVI) benzo[*g,h,i*]perylene. Adapted from (Yan et al., 2004).

shoes, sports item, *etc* (Fisner et al., 2013). The source of PAHs in these products is due to the use of tar oil as an extender oil in making plastics with desired elasticity. Coal briquettes, being used as a fuel in industries and residential purposes, contain large amount of PAHs due to the presence of coke, peat, charcoal and binding agents such as tar, pitch or bitumen (EPA, 2008). Further, high contents of PAHs have been found in paints and coating materials used for protecting hydraulic equipment, pipes, steel piling, etc (EPA, 2008). Creosate, a well-known PAH is widely used for timber protection against environmental degradation. While the use of creosote is becoming increasingly restricted/prohibited in gardens, parks and playground; the major creosote contamination (approximately one-third) in the environment occurs from railway sleepers treated with creosote with an average service life of 26 years (Kohler et al., 2000).

3.2. Transport and fate of PAHs in aquatic ecosystems

In today's world, one of the prime food production sectors is aquaculture. To increase the production of aquatic species, farmers are taking a number of approaches, including adding protein rich diet, increased rate of water exchange, and also an increased use of chemicals and drugs that promote the growth of target organisms. However, addition of these chemicals and growth-enhancers in modern aquaculture is now considered as the prime source of water pollution. Besides these, addition of wastewater from sewage treatment plants and industries remain the traditional major sources of pollutants (metals, metalloids and synthetic organic chemicals, such as surfactants, PAHs, phthalates, pesticides, pharmaceutical compounds and their degradation products) in natural water bodies. Presence of these xenobiotic elements results in disease outbreaks, eco-pollution, eutrophication and inhibition of important biological processes such as nitrogen fixation (Dokianakis et al., 2006). In recent times, it has been found that with an increase in land-based activities there is a concomitant increase in the contamination of PAHs in the aquatic environment. For instance, the global discharge of PAHs in aquatic ecosystem was estimated to be over 80,000 tons per annum in 2002 (Wright and Welbourn, 2002). PAHs can persist in water for extremely long time, as they are less sensitive to photooxidation in water than in air due to several factors including hydrophobicity and turbulence-induced dilution effects. The point sources of PAHs in the aquatic environment include direct discharge from municipal wastewater facilities and industrial outfalls (Abdel-Shafy and Mansour, 2016), whereas the nonpoint sources include urban and surface water runoff from various land use types and atmosphere. The distribution and fate of different types of PAHs are greatly influenced by their relative solubility and hydrophobicity (Fig. 2) (Scott et al., 2012). In an aquatic environment, PAHs get rapidly absorbed onto particulate matter and as a result higher concentrations of PAHs are generally found in sediments and the lowest in surface water and water columns (Stigliani et al., 1993). Further, pyrogenic PAHs have been observed to dominate in sedimentary particles over petrogenic PAHs (Stogiannidis and Laane, 2015). This may be due to the higher degree of resistance of pyrogenic PAHs against natural photochemical oxidation and microbial degradation. Importantly,

Table 1
Physiochemical and toxicological parameters of US EPA enlisted PAHs.

PAHs	Ring No.	MW	MP	BP	S (mg L^{-1})	Vp (Pa)	H (Pa m^3 mol^{-1})	Log K_{ow}	BCF	FCV (μg L^{-1})	References
Naphthalene	2	128	80	218	31	10.4	43.01	3.37	2.33	193.5	(EPA, 2000; Latimer and Zheng, 2003; Mackay et al., 1992)
Acenaphthylene	3	150	92	207	16.1	0.9	8.4	4.00	2.79	306.9	(EPA, 2000; Latimer and Zheng, 2003; Mackay et al., 1992)
Acenaphthene	3	154.2	95	279	3.9	0.29	18.5	3.92	2.63	55.85	(EPA, 2000; Humans, 2010; Mackay et al., 1992)
Fluorene	3	166.2	116	295	1.68	0.08	9.81	4.18	3.10	39.30	(EPA, 2000; Humans, 2010; Mackay et al., 1992)
Phenanthrene	3	178.2	100	340	1.18	0.016	4.29	4.57	3.27	19.13	(EPA, 2000; Humans, 2010; Mackay et al., 1992)
Anthracene	3	178.2	216	342	0.043	8.0×10^{-4}	5.64	4.45	3.14	20.73	(EPA, 2000; Humans, 2010; Mackay et al., 1992)
Fluoranthene	4	202.3	110	384	0.26	0.00123	1.96	5.20	2.87	7.11	(EPA, 2000; Humans, 2010; Mackay et al., 1992)
Pyrene	4	202.3	150	404	0.135	0.0006	1.71	5.00	3.41	10.11	(EPA, 2000; Humans, 2010; Mackay et al., 1992)
Benzo[a]anthracene	4	228.3	160	435	0.0009	2.80×10^{-5}	1.22	5.91	4.13	2.23	(EPA, 2000; Humans, 2010; Latimer and Zheng, 2003; Mackay et al., 1992)
Chrysene	4	228.3	254	448	0.00179	5.70×10^{-7}	0.53	5.86	3.19	2.04	(EPA, 2000; Humans, 2010; Latimer and Zheng, 2003; Mackay et al., 1992)
Benzo[b]fluoranthene	5	252.3	168	481	0.0015	5.0×10^{-7}	0.051	5.78	2.58	0.68	(EPA, 2000; Humans, 2010; Latimer and Zheng, 2003; Mackay and Hickie, 2000; Mackay et al., 1992)
Benzo[k]fluoranthene	5	252.3	217	480	0.0008	5.20×10^{-8}	0.044	6.11	2.67	0.64	(EPA, 2000; Humans, 2010; Latimer and Zheng, 2003; Mackay et al., 1992)
Benzo[a]pyrene	5	252.3	178	310	0.0038	7.00×10^{-7}	0.034	6.35	3.74	0.96	(EPA, 2000; Humans, 2010; Latimer and Zheng, 2003; Mackay et al., 1992)
Dibenz[a,h]anthracene	5	278.4	266	524	0.0005	3.70×10^{-10}	–	6.75	3.91	0.28	(EPA, 2000; Humans, 2010; Latimer and Zheng, 2003; Mackay et al., 1992)
Benzo[g,h,i]perylene	6	276.3	278	500	0.00026	1.66×10^{-8}	0.027	6.90	5.00	0.44	(EPA, 2000; Humans, 2010; Latimer and Zheng, 2003; Mackay et al., 1992)
Indeno[1,2,3-c,d]pyrene	6	276.3	163	536	0.00019	1.30×10^{-8}	0.029	–	–	0.28	(EPA, 2000; Humans, 2010; Latimer and Zheng, 2003; Mackay et al., 1992; Yusà et al., 2006)

MW - molecular weight; MP - melting point; BP - boiling point; S - water solubility; Vp - vapor pressure; H – Henry's law constant; K_{ow} - octanol-water partition coefficient; BCF - bioconcentration factor; FCV - final chronic value.

when PAHs are discharged into the aquatic environment from different sources, they get localized in rivers, estuaries, and costal marine water alike. In this context, it may be noted that the major sources of PAHs in inland aquatic ecosystems are different from those in marine aquatic ecosystems. The PAHs in marine aquatic ecosystem typically accumulate naturally from atmospheric deposition of PAHs emitted through pyrogenic activities (e.g. volcanic eruption). Additional petrogenic activities, such as petroleum spill, oil seepage, *etc* are further increasing the PAH levels in marine aquatic ecosystems. In contrast, as many thermal power plants are situated on the banks of major riverine ecosystems, the likelihood of pyrogenic PAHs occurrence remains higher in adjacent rivers (Agarwal et al., 2006). Since estuaries are important breeding ground for several fish species, presence of PAHs in these environments leads to bioaccumulation of this xenobiotic in the developing fish, causing aquatic toxicity. In addition to bioaccumulation, another important aspect worth consideration is the biomagnification of PAHs through the aquatic food chain. Bioconcentration issues associated with PAHs through trophic transfer via aquatic food chain have not only been a subject of scientific interest, they have also started to attract the attention of government bodies (Depree and Ahrens, 2007). Scientific investigations have revealed that the biomagnification of PAHs in aquatic food chain is highly complex. For instance, biomagnification studies of benzo(a)pyrene and 7,12-dimethyl-benz(a)anthracene across the food chain of *Dunaliella tertiolecta* (a microalga), *Mytilus galloprovincialis* (a mussel) and *Dicentrarchus labrax* (a fish) food chain system showed higher accumulation of these PAHs in mussels compared to fish (D'adamo et al., 1997). Another study noted similar observations where the concentrations of PAHs followed a reverse order with the increasing trophic level, such that PAHs concentrations were found to be lower in decapods and fish than in mollusks (Takeuchi et al., 2009). More recent studies indicate that the bioaccumulation of PAHs in fish is directly correlated with the PAH concentration in aquatic plants, reflecting that PAHs in fish are most likely predominantly adsorbed from aquatic plants rather than directly from water (Zhang et al., 2015).

4. Aquatic eco-toxicity of PAHs

PAHs show moderate to high acute toxicity in aquatic organisms depending upon the type of PAH and the organism involved. Generally, PAHs are found to be highly toxic to zooplanktons with LC_{50} values (lethal concentration that kills 50% of the population) approaching parts per billion concentrations (ppb or μg L^{-1}). For instance, benzo[*a*]pyrene was found to have LC_{50} values of 5 μg L^{-1} and 58 μg L^{-1} against *Daphnia pulex* and *Eurytemora affinis*, respectively. Similar ppb level toxicity was observed against *Ceriodaphnia reticulate* (LC_{50} − 4.3 μg L^{-1}) and *Daphnia magna* (LC_{50} − 4.7 μg L^{-1}) (Ikenaka et al., 2013). In contrast, PAHs have been observed to show mixed effects on phytoplanktons, such that they are extremely toxic against certain phytoplanktons, whereas other phytoplankton species have higher tolerance levels. For instance, benzo[*a*]pyrene was notably toxic against *Scenedesmus acutus* (LC_{50} − 5 μg L^{-1}) and *Pseudokirchneriella subcapitata* (LC_{50} − 15 μg L^{-1}), however their toxicity was lower against *Anabaena flosaquae* and *Chlamydomonas reinhardtii* (LC_{50} − 4000 μg L^{-1}) (Schoeny et al., 1988). Even at sub-toxic concentrations, PAHs can cause severe growth reduction in the planktonic species including hampering metabolic activities such as enzyme inhibition, enhanced lipid peroxidation, inhibition of photosynthesis, etc (Othman et al., 2011; Schoeny et al., 1988). The key toxic effects of different types of PAHs on zooplanktons and phytoplanktons are summarised in Table 2 and Table 3, respectively.

Beside the toxic effects on planktons, research on

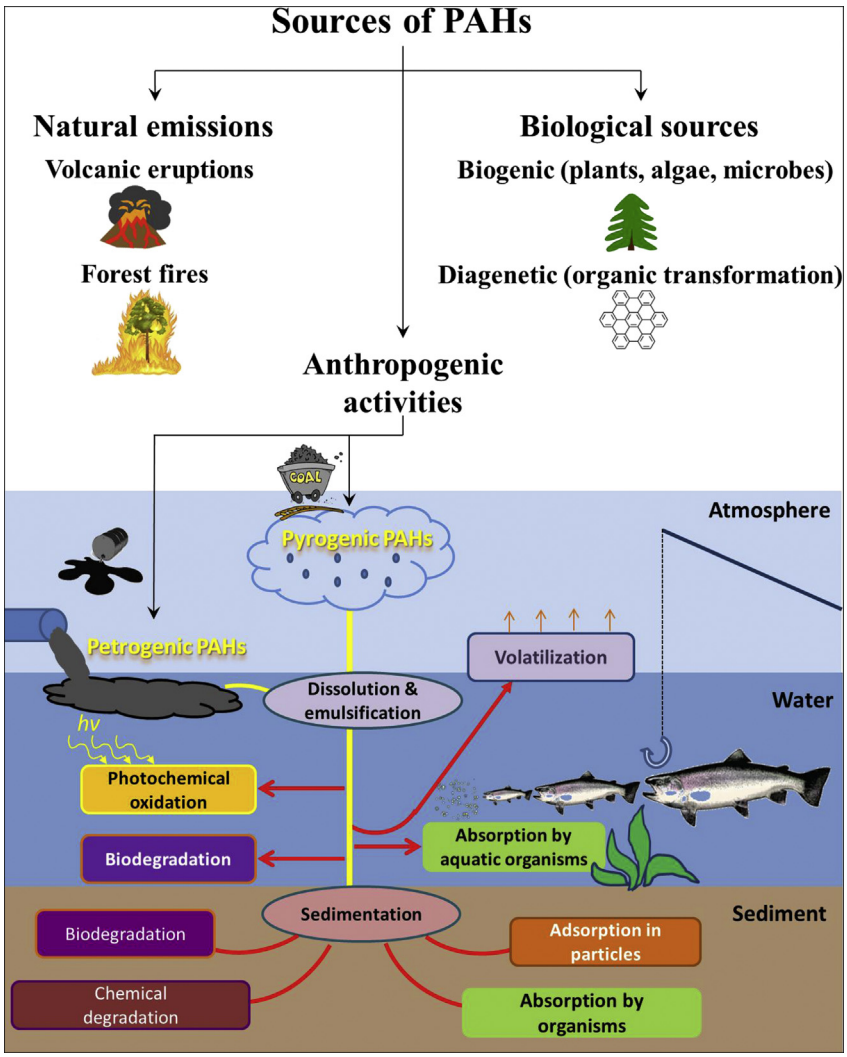

Fig. 2. Major sources of PAHs in the environment and their distribution and fate in the aquatic ecosystem. Adapted with modifications from (Abdel-Shafy and Mansour, 2016; Ligaray et al., 2016).

bioconcentration and bioaccumulation of PAHs in planktonic species is gaining considerable momentum in view of the role of these planktons as a food source to fish (Almeda et al., 2013; D'adamo et al., 1997). PAHs can impair the reproductive health of higher order animals, thus threatening species survival. One of the key mechanisms of their action involves disruption of the normal metabolism of sex hormone (including gonadotropins) in fish, birds and mammals even at extremely low concentrations. This leads to dysfunctioning of reproductive processes through fertility reduction, alteration of sexual behaviour, viability of offspring and hatch rate (Crews et al., 1995). Certain PAHs are observed to show sex-specific bioaccumulation. For instance, anthracene was found to get concentrated more in the ovaries than in the testes of Fathead minnows (Hall and Oris, 1991). Endocrine dysfunction and reduced gonad size has been observed in yellow perch fish (*Perca avescens*) exposed to St. Lawrence River sediment contaminated with PAHs and polychlorinated biphenyls (PCBs) (Hontela et al., 1995). On the other hand, increased liver somatic index (LSI) was observed in hardhead catfish and sunfish collected from freshwater creeks contaminated with PAHs and PCBs (East Tennessee, USA), and from the estuarine and marine waters contaminated with PAHs and cadmium (Mississippi Sound, USA) (Everaarts et al., 1993). Similarly, a two-fold increase in LSI was also seen in bluegill sunfish collected from the PAHs-contaminated sediments (Theodorakis et al., 1992). The metabolic toxicity profile of PAHs is wide-ranging. As such, a number of other PAH-induced physiological effects, such as elevated hepatosomatic index in brown bullhead (Baumann et al., 1991); increased hemoglobin concentration in sunfish (Everaarts et al., 1993); and decreased hemoglobin concentration in hardhead catfish (Everaarts et al., 1993) provide some indications on PAH toxicity in aquatic organisms.

These observations on the toxic effects of PAHs accumulated in natural aquifers have also led to concerted efforts, in which fish were exposed to specific PAH compounds in a controlled environment to assess their toxicity. For instance, naphthalene exposure to fish (4 mg L^{-1}) increased the levels of blood cortisol and glucose, leading to osmoregulatory imbalance (Levitan and Taylor, 1979). Similarly, exposure of other PAHs to fish led to elevated concentrations of PAH metabolites in bile and stomach, increased levels of DNA adducts in liver, and induction of hepatic CYP1A activity (Stehr et al., 2000). The toxic effects of different PAHs on fish species are summarised in Table 4.

5. Biosensors for the detection and monitoring of PAHs

The adverse effects of PAHs towards the environment as well as

Table 2
Toxic effect of PAHs on zooplankton species.

PAHs	Zooplankton	Toxic effect	Ref
Anthracene	*Artemia salina*	Acute toxicity, LC_{50} 1009.5 ± 37.5 μg L^{-1}	(Wang et al., 2008)
	Mysidopsis bahia	Acute toxicity, LC_{50} 535 μg L^{-1}	(Pelletier et al., 1997)
Naphthalene	*Paracartia grani*	Acute toxicity, LC_{50} 2523 μg L^{-1}	(Calbet et al., 2007)
	Oithona davisae	LC_{50} > 10 mg L^{-1}	(Saiz et al., 2009)
Benzo[*a*]pyrene	*Daphnia pulex*	Acute toxicity	(Forget-Leray et al., 2005; Trucco et al., 1983)
	Eurytemora affinis	Acute toxicity, EC_{50} 58 μg L^{-1}	(Forget-Leray et al., 2005; Trucco et al., 1983)
	Ceriodaphnia reticulata	Acute toxicity, EC_{50} 4.3 μg L^{-1}	(Ikenaka et al., 2013)
	Daphnia magna	Acute toxicity, EC_{50} 4.7 μg L^{-1}	(Ikenaka et al., 2013)
	Eurytemora affinis	Bioconcentration	(Cailleaud et al., 2009)
Phenanthrene	*Pseudodiaptomus marinus*	Bioaccumulation (BAF), Log BAF 3.86; Bioconcentration (BCF), Log BCF 3.8	(Arias et al., 2016)
	Eurytemora affinis	Bioconcentration	(Cailleaud et al., 2009)
	Paracartia(acartia) grani	Bioaccumulation & Bioconcentration	(Berrojalbiz et al., 2009)
	Daphnia magna	Inhibition of superoxide dismutase	(Zhang et al., 2014)
	Acartia tonsa	EC_{50} 105.87 μg L^{-1}	(Bellas and Thor, 2007)
	Artemia salina	LC_{50} 1320.7 ± 19.8 μg L^{-1}	(Wang et al., 2008)
Fluoranthene	*Pseudodiaptomus marinus*	Bioaccumulation (BAF), Log BAF 4.13; Bioconcentration (BCF), Log BCF 4.27	(Arias et al., 2016)
	Acartia tonsa	EC_{50} 120.14 μg L^{-1}	(Bellas and Thor, 2007)
	Tisbe battagliai	LC_{50} 101.1 μg L^{-1}	(Barata et al., 2002)
	Artemia salina	LC_{50} 1430.5 ± 13.4 μg L^{-1}	(Wang et al., 2008)
Pyrene	*Pseudodiaptomus marinus*	Bioaccumulation (BAF), Log BAF 4.95; Bioconcentration (BCF), Log BCF 4.72	(Arias et al., 2016)
	Eurytemora affinis	Bioconcentration	(Cailleaud et al., 2009)
	Paracartia (acartia) grani	Bioaccumulation & Bioconcentration	(Berrojalbiz et al., 2009)
	Acartia tonsa	EC_{50} > 129.45 μg L^{-1}	(Bellas and Thor, 2007)
	Artemia salina	LC_{50} 1770.6 ± 213.1 μg L^{-1}	(Wang et al., 2008)
Chrysene	*Eurytemora affinis*	Bioconcentration	(Cailleaud et al., 2009)

animal life have led to efforts in development of diagnostic platforms for the detection of these compounds. Traditional methods of detecting these compounds include chromatographic techniques, such as, high performance liquid chromatography (HPLC) coupled with fluorometric probes, photodiode-array, ultraviolet or mass spectroscopy detector; gas chromatography (GC) combined with flame ionisation or mass spectroscopy detector; and superficial fluid chromatography with ultraviolet or mass spectroscopy detector (Ahmad and Moore, 2009; Manoli and Samara, 1999; Pandey et al., 2011). Though these methods show excellent specificity and sensitivity towards the detection of PAHs, temporal and spatial heterogeneity of PAH distribution in aquatic environments such as lakes, rivers and coastal areas, complicate the sampling process during the analysis (Manoli and Samara, 1999). Additionally, the monitoring of a significant number of samples obtained from random locations remains a mandatory prerequisite to obtain

Table 3
Toxic effect of PAHs on phytoplankton species.

PAHs	Phytoplankton	Toxic effect	Ref
Anthracene	*Scenedesmus subspicatus*	Acute toxicity, EC_{50} 1.04 μg L^{-1}	(Djomo et al., 2004)
	Phaeodactylum tricornutum	Growth inhibition, EC_{50} 123 ± 5.5 μg L^{-1}	(Wang et al., 2008)
Naphthalene	*Chlorella vulgaris*	Oxidative damage	(Kong et al., 2010)
	Calanus finmarchicus	Acute toxicity	(Falk-Petersen et al., 1982)
	Ditylum brightwellii	Acute toxicity, EC_{50} 1011 μg L^{-1}	(Ozhan and Bargu, 2014)
	Heterocapsa triquetra	Acute toxicity, EC_{50} 1653 μg L^{-1}	(Ozhan and Bargu, 2014)
	Scenedesmus subspicatus	Acute toxicity, EC_{50} 68.21 μg L^{-1}	(Djomo et al., 2004)
Benzo[*a*]pyrene	*Scenedesmus acutus, Pseudokirchneriella subcapitata, Anabaena flosaquae, Chlamydomonas reinhardtii*	Acute toxicity, EC_{50} 5–4000 μg L^{-1}	(Schoeny et al., 1988)
	Ditylum brightwellii	Acute toxicity, EC_{50} 1.13 μg L^{-1}	(Ozhan and Bargu, 2014)
	Heterocapsa triquetra	Acute toxicity, EC_{50} 7.02 μg L^{-1}	(Ozhan and Bargu, 2014)
	Scenedesmus subspicatus	Acute toxicity, EC_{50} 1.48 μg L^{-1}	(Djomo et al., 2004)
	Thalassiosira pseudonana	Growth inhibition, EC_{50} 55.24 μg L^{-1}	(Bopp and Lettieri, 2007)
Benz[*a*]anthracene	*Nannochloris* sp., *Picochlorum* sp., *Isochrysis galbana, Dunaliella tertiolecta, Chaetoceros muelleri, Phaeodactylum tricornutum, Alexandrium catenella*	Inhibition of photosynthesis, Acute toxicity, EC_{50} 208 –1825 μg L^{-1}	(Othman et al., 2011)
Phenanthrene	*Rhodomonas salina*	Bioconcentration	(Berrojalbiz et al., 2009)
	Scenedesmus subspicatus	Acute toxicity, EC_{50} 50.24 μg L^{-1}	(Djomo et al., 2004)
	Phaeodactylum tricornutum	Growth inhibition, EC_{50} 154 ± 3.1 μg L^{-1}	(Wang et al., 2008)
Pyrene	*Phaeodactylum tricornutum*	Acute toxicity, EC_{50} 68–70 ppb	(Okay et al., 2002)
	Rhodomonas salina	Bioconcentration	(Berrojalbiz et al., 2009)
	Scenedesmus subspicatus	Acute toxicity, EC_{50} 18.72 μg L^{-1}	(Djomo et al., 2004)
	Thalassiosira pseudonana	Growth inhibition, EC_{50} 260.3 μg L^{-1}	(Bopp and Lettieri, 2007)
	Phaeodactylum tricornutum	Growth inhibition, EC_{50} 119 ± 1.2 μg L^{-1}	(Wang et al., 2008)
Fluoranthene	*Nannochloris* sp., *Picochlorum* sp., *Isochrysis galbana, Dunaliella tertiolecta, Chaetoceros muelleri, Phaeodactylum tricornutum, Alexandrium catenella*	Inhibition of photosynthesis, Acute toxicity, EC_{50} 54 –1605 μg L^{-1}	(Othman et al., 2011)
	Thalassiosira pseudonana	Growth inhibition, EC_{50} 1031 μg L^{-1}	(Bopp and Lettieri, 2007)
	Phaeodactylum tricornutum	Growth inhibition, EC_{50} 103 ± 9.1 μg L^{-1}	(Wang et al., 2008)

Table 4
Toxic effect of PAHs on fish species.

PAHs	Fish species	Toxic effect on fish	Ref
Naphthalene	Fathead minnows (*Pimephales promelas*) and rainbow trout (*Oncorhynchus mykiss*)	Growth reduction, increased respiratory burst activity	(DeGraeve et al., 1982)
	Pink Salmon (*Oncorhynchus gorbuscha*);	Growth reduction	(Moles and Rice, 1983)
	European eel (*Anguilla anguilla* L)	Growth reduction	(Ahmad et al., 2003)
Acenaphthene	Fathead minnows (*Pimephales romelas*)	Lethargic behaviour and lack of alarm response, LC_{50} 1600 μg L^{-1}	(Cairns and Nebeker, 1982)
	Channel catfish (*Ictalurus punctatus*)	LC_{50} 1720 μg L^{-1}	(Holcombe et al., 1983)
	Rainbow trout (*Oncorhynchus mykiss*)	LC_{50} 670 μg L^{-1}	(Holcombe et al., 1983)
	Brown trout (*Salmo trutta*)	LC_{50} 580 μg L^{-1}	(Holcombe et al., 1983)
Fluorene	Bluegill (*Lepomis macrochirus*)	Abnormality in swimming behaviour	(Little and Finger, 1990)
	English sole (*Parophrys vetulus*)	Liver lesions	(Myers et al., 1991)
	Zebrafish (*Danio rerio*)	Defect in cardiac Function	
Phenanthrene	Zebrafish (*Danio rerio*)	Defect in cardiac Function	(Incardona et al., 2004)
	Gold fish (*Carassius auratus*)	Oxidative stress	(Sun et al., 2006)
	Golden grey mullet (*Liza aurata*)	Oxidative damage	(Oliveira et al., 2008)
	Japanese medaka (*Oryzias latipes*)	Prolonged hatching duration	(Horng et al., 2010)
Anthracene	Bluegill sunfish (*Lepomis macrochirus*)	Irritation and hypoxia, LC_{50} 11.9 μg L^{-1}	(Oris et al., 1984)
	Fathead minnows (*Pimephales promelas*)	Photo-induced toxicity, Reduction in per cent hatching	(Hall and Oris, 1991; Oris et al., 1990)
	Milkfish (*Chanos chanos*)	Oxidative stress, neurotoxicity	(Palanikumar et al., 2012)
Fluoranthene	Fathead minnows (*Pimephales promelas*)	Acute photoinduced toxicity, LC_{50} 12.2 μg L^{-1}	(Spehar et al., 1999; Weinstein and Oris, 1999)
	Rainbow trout (*Oncorhynchus mykiss*)	Acute UV induced toxicity, LC_{50} 7.7 μg L^{-1}	(Spehar et al., 1999)
	Bluegill (*Lepomis macrochirus*)	Acute UV induced toxicity, LC_{50} 12.3 μg L^{-1}	(Spehar et al., 1999)
	Sheepshead minnow (*Cyprinodon variegatus*)	Acute UV induced toxicity, LC_{50} 159 μg L^{-1}	(Spehar et al., 1999)
	Inland silverside (*Menidia beryllina*)	Acute UV induced toxicity, LC_{50} 30 μg L^{-1}	(Spehar et al., 1999)
	Winter flounder (*Pleuronectes americanus*)	Acute UV induced toxicity, LC_{50} 0.1 μg L^{-1}	(Spehar et al., 1999)
Pyrene	Zebrafish (*Danio rerio*)	Defect in cardiac function	(Incardona et al., 2004; Zhang et al., 2012)
	Fathead minnow (*Pimephales promelas*)	Photoinduced toxicity	(Kagan et al., 1987)
	Common goby (*Pomatoschistus microps*)	Inhibition of acetylcholinesterase activity	(Oliveira et al., 2013)
Benzo[*a*]pyrene	Milkfish (*Chanos chanos*)	Increase lipid peroxidation and catalase activity, inhibition of acetylcholinesterase	(Palanikumar et al., 2012)
	Zebrafish (*Danio rerio*)	Decrease in ovarian somatic index, reduction in egg count, increase in Cytochrome P4501A1 expression	(Hoffmann and Oris, 2006)
	Japanese medaka (*Oryzias latipes*), guppy (*Poecilia reticulata*)	hepatocellular lesions, carcinogenic effects	(Hawkins et al., 1988)
	Killifish (*Fundulus heteroclitus*)	Hepatocellular carcinomas	(Wills et al., 2010)
Benzo[*k*]fluoranthene	Northern pike (*Esox lucius*)	Formation of DNA adducts	(Ericson and Balk, 2000)
	Zebrafish (*Danio rerio*)	Induction of *cyp1a1* gene encoding for cytochrome P450	(Barranco et al., 2017)
	Crucian Carp (*Carassius carassius*)	Enhanced liver 7-ethoxyresorufin-O-deethylase activity	(Ding et al., 2014)

reliable information about PAH concentrations. However, the unit cost per assay, high capital cost, time-intensiveness, and reliance on technical expertise pose practical limitations in employing traditional analytical techniques for reliable real-time analysis of PAH-contaminated samples. Importantly, the time gap between sample collection and sample analysis is a critical factor, as it influences the accuracy of detection. This is due to the requirement of maintaining the original integrity of the collected sample that could change as a function of storage time due to lipophilic and volatile nature of these PAHs. Therefore, there is a growing interest to develop simple, cost-effective, rapid and field portable point-of-care (POC) biosensors that could identify the presence of PAHs, preferably in a real-time scenario.

A biosensor may be defined as an analytical device that can either qualitatively or quantitatively detect the presence of the target analyte, including small molecules, macromolecular biomolecules or whole cells (Perumal and Hashim, 2014). A sensor is typically consisted of three main components namely a molecular recognition element (MRE), a transducer and a detector (Fig. 3) (Perumal and Hashim, 2014; Rahaie and Kazemi, 2010). When a complex sample containing the target molecule comes in contact with the sensor, the MRE selectively identifies the target analyte, and therefore brings in an element of specificity/selectivity to the sensor, making them a critical element in biosensors. This MRE can belong to different classes, ranging from antibodies, enzymes and proteins (as in enzyme-linked immunosorbent assays - ELISA); to lectins and carbohydrates (as in lectin binding assays – LBAs); to nucleic acids (as in polymerase chain reaction – PCR – to recognise the complementary DNA/RNA); and to aptamers (small polynucleotide sequences with high target specificity) (Perumal and Hashim, 2014; Saha et al., 2012). Each of these MREs offers their own distinct advantages and limitations, as discussed later in this review. In terms of the sensor operation, when the target analyte interacts with MRE bound to the sensor, a primitive signal is generated in a target-concentration dependent manner. The nature of this signal depends on the choice of the transducer component, which is responsible for converting this signal into a quantifiable readout that is finally captured by a detector.

Biosensors are typically categorised based on either the utilized MRE or the transducer platform. Optical (e.g. colorimetric, fluorometric, luminometric) (Aldewachi et al., 2017; Karim et al., 2018; Le et al., 2017; Lee et al., 2010; Sharma et al., 2014; Singh et al., 2017; Weerathunge et al., 2014; Zohora et al., 2017); spectrometric (e.g. Fourier transform infrared spectroscopy - FTIR, surface enhanced Raman spectroscopy – SERS, surface plasmon resonance - SPR) (Agrawal et al., 2013; Bodelón et al., 2016; Carnovale et al., 2016;

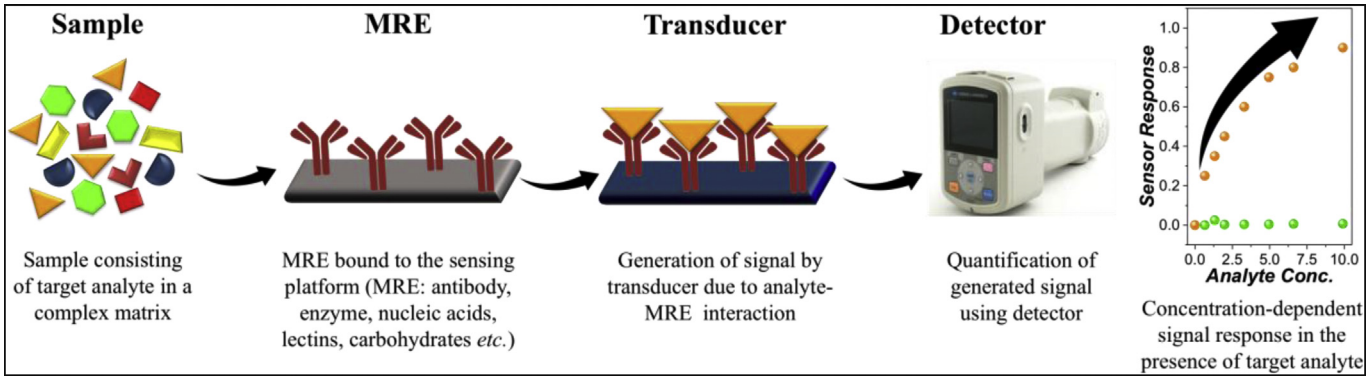

Fig. 3. Different components of a functional sensor ranging from a molecular recognition element (MRE), a transducer element and a detector component, eventually leading to a signal response from a biosensing event.

Kandjani et al., 2014; Masson, 2017; Muhamadali et al., 2016; Selvakannan et al., 2013); conductometric (e.g. amperometric, potentiometric) (Erden and Kılıç, 2013; Ramanathan et al., 2013; Ramanathan et al., 2015; Rathee et al., 2016); and gravimetric (e.g. quartz crystal microbalance – QCM) (Della Ventura et al., 2017; Esmaielzadeh Kandjani et al., 2015; Sabri et al., 2012; Sabri et al., 2011; Sabri et al., 2014; Vashist and Vashist, 2011; Walia et al., 2017b; Walia et al., 2017a) are different types of biosensors depending upon the choice of the transduction mode. In contrast, if classified based on the MRE, these may be classified as immunochemical, enzyme-based, whole cells, DNA and aptasensors (Ahmed et al., 2014; Luong et al., 1997; Perumal and Hashim, 2014). In a typical scenario, since both the MRE and transducer are critical to sensor performance, the final sensor is identified using a terminology that synchronously recognises both these elements. For instance, a colorimetric aptasensor will mean that this sensor utilizes aptamers as the MRE, while the analyte detection mode is through colour production. The subsequent sections of this review discuss the currently available biosensing platforms for PAH detection, and the key features of these biosensors are summarised in Table 5.

5.1. Enzyme-linked immunosorbent assays (ELISA) for PAH detection

Apart from conventional analytical technologies for PAH detection, biosensors fabricated so far for monitoring PAHs are mainly based on immunoassays. Immunoassays are the biochemical tests, which are able to identify the existence of PAHs using high affinity proteins (antibodies) (Knopp et al., 2000). The selectivity, fast response rate, cost effectiveness and the ability to monitor multiple samples simultaneously (multiplexing) has highlighted the importance of these immunoassays for detecting PAHs in different environmental settings (Knopp et al., 2000; Li et al., 2016; Spier et al., 2011). The underlying principle for these immunoassays is based on highly specific interaction of the target PAH analyte with a corresponding antibody, followed by the production of a colorimetric/fluorometric response to allow quantitative determination of PAH.

Competitive ELISA is the most common form of immunoassay employed for PAH detection. Competitive ELISA assay may be considered as a negative assay as in this assay less intense colour is generated in the presence of the analyte in comparison to that in the absence of the analyte (Fig. 4). A competitive ELISA involves exposing the sample containing the analyte (antigen) to an excess of target-specific (primary) antibody. This results in a mixture containing free antibodies and antigen-antibody complexes. When this mixture is exposed to an antigen-coated ELISA plate, the free antibodies from the mixture can then bind to the ELISA plate, whereas the antigen-antibody complexes are washed-off during a subsequent washing step. When this set-up is further exposed to an enzyme-conjugated secondary antibody, it binds to the ELISA plate. In the presence of a suitable substrate, the enzyme is then able to generate a signal by converting the substrate to a colorimetric/fluorometric product. During competitive ELISA, the generation of the oxidised product by the enzyme is inversely proportional to the concentration of the target analyte in the sample and hence the intensity of colour/fluorescence signal acts as an indicator to monitor the amount of the target analyte quantitatively.

Based on the affectivity of competitive ELISA-based immunoassays, US Environmental Protection Agency (EPA) has noted their suitability for monitoring PAHs in soil samples. PAH RISc® (EnSys, Inc.), RaPID-ELISA (Ohmicron, Newtown, PA), *etc.* are some of the commercially available products that are able to detect PAHs in environmental soil samples. A number of research groups have also evaluated the performance in these commercial immunoassays for PAHs detection (Chuang et al., 1998; Krämer, 1998; Nording and Haglund, 2003; Waters et al., 1997). Overall, the comparison data from these studies have shown that immunoassays are indeed very effective for qualitative monitoring of PAHs. However, the use of these kits for precise quantitative analysis of specific PAHs was found challenging, as different antibodies utilized in these kits showed differential binding ability towards different PAHs. This poses a limitation that prior knowledge about the composition of the analyte sample is required with respect to the reference sample present in the immunoassay kits (Nording and Haglund, 2003; Waters et al., 1997).

Among a number of developments, a competitive ELISA assay kit for colorimetric determination of PAHs with 3–6 aromatic rings in soil was reported with 1 ppm limit of detection (LoD) (McDonald et al., 1994). The ability of this test kit for accurately determining PAHs concentrations in soil samples without interference from the soil matrix provides opportunities for rapid screening of a large number of environmental samples (McDonald et al., 1994). The ability to use ELISA-based immunoassays for the determination of pyrene and other homologues of PAHs is also reported (Meng et al., 2015). The sensor showed high sensitivity (LoD of 65.08 pg mL^{-1}) and minimal interference from the matrices of water samples obtained from different sources (tap water, lake water, and mineral water). These, along with good recoveries suggest the potential efficacy of these ELISA-based techniques for detecting pyrene homologues of PAHs in water samples (Meng et al., 2015).

Immunoassay kits have also been employed for the determination of PAHs in urine and haemolymph samples of vertebrates

Table 5
Different biosensing platforms for detection of PAHs.

MRE	Target analyte	Detection limit (LoD)	Pros	Cons	Real-time application/ recommendation	Ref
Enzyme-linked immunosorbent assays (ELISA)						
Antibody	3- and 4- ringed aromatic compounds and most of the 5- and 6-ringed aromatics	1 ppm LoD	• Good accuracy, sensitivity and specificity towards PAHs detection • Simple and fast (analysis time less than 25 min) • Good field compatibility for real-time application due to no or minimal effect from soil matrix	• The need of sample treatments before sensing PAH using immunoassay	• Used for monitoring PAHs present in soil samples	(McDonald et al., 1994)
Antibody	1-nitropyrene		• Simple, fast and cost-effective method	• Six fold higher reading in comparison to HPLC. However the use of clean-up process reduced this over-estimation by 1.6 fold. • Cross reactivity with similar analogues (2-nitropyrene and 2-nitrofluoranthene).	• Suitable for general screening of diesel emission	(Zühlke et al., 1998)
Monoclonal antibody	Four-to six-ring aromatic PAHs. The highest response was observed in the presence of benzo[*a*]pyrene	LoD of 30 pg per well for benzo [*a*]pyrene	• Cost-effective method which could detect samples in parallel. • The sensor showed good tolerance towards certain organic solvents.	• The comparison of the detection with HPLC revealed that the ELISA had nearly five-fold higher values due to structurally similar compounds interacting with antibodies. • Broad specificity towards PAHs and suitable as a PAHs screening method	• The obtained results suggested the suitability of this method as a screening method of PAHs in air samples	(Scharnweber et al., 2001)
Monoclonal antibody	Benzo[*a*]pyrene	LoD of 24 ng L^{-1}	• The pH, ionic strength and inorganic ions had minimal effect towards the used antibody in this ELISA • Ability to use the sensing approach for monitoring portable water without any pre-treatments • Sensing approach was robust and resulted in reproducible results	• Among the tested PAHs chrysene, indeno[*1,2,3-c,d*] pyrene, and benzo[*b*] fluoranthene showed greater than 20% cross reactivity • Overestimation of results when tested with spiked river and lake water samples due to matrix effect	• Used to investigate the benzo [*a*]pyrene present in spiked tap, river and lake water samples • The achieved results during real-time tap water sample testing highlighted the ability to use this method for monitoring PAHs in drinking water	(Matschulat et al., 2005)
Monoclonal antibody	Highly specific towards pyrene and related PAHs namely chrysene, benzo[*a*]pyrene, benzo[*a*]anthracene and indeno [*1,2,3-c,d*]pyrene	Pyrene, chrysene, benzo[*a*] pyrene, benzo[*a*]anthracene, and indeno[*1,2,3-c,d*]pyrene showed detection limit of 65.08, 21.41, 5.24, 301.05, and 147.79 pg mL^{-1} respectively	• Detection limits of the method were higher than the reported HPLC and GC/MS methods • Highly specific towards pyrene and other equivalent PAHs and thereby allowing the method to use as a screening method for monitoring these compounds among the available two- and three-ring PAHs	• The requirement of sophisticated methods for compound-specific detection	• Method was used to monitor pyrene and other homologues of PAHs present in spiked tap, lake and mineral water samples • Good recoveries and reproducibility in results suggested the ability to use this method for testing real-time water samples with less interference from the matrix	(Meng et al., 2015)

Monoclonal antibody	2-hydroxybiphenyl and benzo [*a*]pyrene	0.1−1000 ppb and 0.1−300 ppb range when detecting 2-hydroxybiphenyl and benzo[*a*] pyrene respectively	• The simultaneous detection of both components highlighted the multiplexing ability of this biosensor • Highly sensitive and reusable biosensor which required less sample volume for analysis (300 μl) • Fast response during detection (Response time was 15 min)	• Real-time application in different samples (food, medical diagnosis) is required to determine the matrix effect of this sensing approach	• Suggested to use for food and medical diagnostic in field	(Gobi and Miura, 2004)
Antibody	Phenanthrene	LoD of 1.4 ppb Linear range of 2−100 ppb	• Rapid and easy to use method which could be potentially used in point of care devices • Reasonably low volume of sample required for analysis • Good reproducibility and repeatability during sensing events	• No information available related to the specificity of the developed sensor	• Analysis of spiked phenanthrene content in river, tap and sea water • The accuracy in the results suggested the ability to use this approach for evaluating water quality	(Moore et al., 2004)
Electrochemical biosensors						
Antibody	PAHs	LoD of 0.02 ppb; linear operational range of 0.05 −1 ppb	• The sensitivity of the method was at least 40 fold lower than the commercially available RaPID assay • The LoD was lower than the set standard by EPA for Method 8310 and other reported method for PAHs sensing • The operation of sensor without the use of organic solvents provides eco-friendly method over other available analytical method for PAH detection • Good recovery was obtained during the testing of spiked water samples with respect to the conventional ELISA method • The developed biosensor was simple and fast in response (analysis time 50 min)	• No information was found to the specific PAH used in the study and hence probably this is a general method which is suitable for screening PAHs	• Method was directly used to determine the spiked PAH in untreated tap water samples	(Lin et al., 2007)
Antibody	benzo[*a*]pyrene	LoD of 4 pM Detection range from 8 pM to 2 nM	• Good sensor response in terms of reproducibility, precision and stability • Broad dynamic linear range • High sensitivity due to the dual amplification strategy • Potential to use this approach for multiple detection of target analyte	• Lack of specificity data for the developed sensor platform	• The sensor was used to evaluate benzo[*a*]pyrene present in spiked water samples	(Lin et al., 2012)

(*continued on next page*)

Table 5 (*continued*)

MRE	Target analyte	Detection limit (LoD)	Pros	Cons	Real-time application/ recommendation	Ref
			simultaneously (multiplexing)			
Antibody	Phenanthrene	LoD of 0.8 ng mL^{-1} (800 ppt) and linear range of 0.5 −45 ng mL^{-1} during indirect co-exposure competition assay	• Comparatively less analysis time due to indirect co-exposure • Highly sensitive than the indirect competition and displacement assays • Good method to determine the total amount of PAHs present in samples • Ability to use this concept for portable device fabrication	• Cross reactivity with other structurally similar PAHs • The requirement of precise method for compound-specific PAH detection • The sensitivity of the sensor which obtained during the real-time sample testing was less sensitive to original values	• The method was used to assess phenanthrene in spiked river and tap water samples	(Fahnrich et al., 2003)
Surface plasmon resonance (SPR) biosensors						
Monoclonal antibody	2-hydroxybiphenyl and benzo [*a*]pyrene	0.1−1000 ppb and 0.1−300 ppb linear range when detecting 2-hydroxybiphenyl and benzo[*a*] pyrene respectively and 0.1 ppb LoD for both compounds	• Rapid response (analysis time 15 min) • The ability to reuse the chip more than 50 times with less than 10% decrement in signal	• No results were reported with respect to the specificity of the sensor	• Real samples not demonstrated	(Gobi et al., 2003)
Antibodies	Benzo[*a*]pyrene, atrazine, 2,4-dichlorophenoxyacetic acid and 4-nonylphenol	LoD for benzo[*a*]pyrene, atrazine, 2,4-dichlorophenoxyacetic acid and 4-nonylphenol was 0.05, 0.07, 0.16 and 0.26 ng mL^{-1}, respectively	• Simultaneous detection of multiple endocrine disrupting chemicals • These LoDs were lower than the limits set by regulatory bodies in USA and EU • Fast response (15 min) • Good reusability	• Cross-reactivity limits the ability to use this sensor for compound specific detection when the sample contains mixed analytes	• Real samples not demonstrated	(Dostálek et al., 2007)
Monoclonal antibody 2G8	3- to 5- ring unsubstituted and methylated PAHs	LoD of 0.2 μg L^{-1}	• Low sample volume for analysis • High sensitivity • Low cost method • Comparatively less analysis time • The identified 2G8 antibody showed comparable results to commercially available antibodies namely 10D10 and 4D5	• The requirement of compound specific method such as GC-MS to identify the precise 3−5 ring PAH	• Used for monitoring of PAHs present in water soluble fractions obtained from oil and creosote to sediment pore water samples • The received results were comparable to GC-MS	(Li et al., 2016)
Fluorescence polarization immunoassays (FPIA)						
Monoclonal antibody BAP-13	small and large PAHs	0.9, 1.1, and 3.4 ng mL^{-1} for benzo[*a*]pyrene, naphthalene, and anthracene, respectively	• Simple, fast, sensitive, and low cost technique for detecting PAHs • Specific individual PAHs as well as group- and class-specific PAHs analysis • Good recoveries and accuracy in detection when testing real-time water samples and proposed as a method of screening to evaluate the quality of surface water	• Potentially low ambient stability of antibodies	• Analysed the surface water samples spiked with benzo [*a*]pyrene, one of the most toxic PAHs	(Yu Goryacheva et al., 2007)

Whole cell bacterial biosensors					
Recombinant bioluminescent *E. coli* GC2 (*lac::luxCDABE*)	Phenanthrene	2.06 ppm	• The sensing platform is suitable as an in-situ soil biosensor for screening hydrophobic soil contaminants • The designed biosensor is easy to use and showed rapid responses with reproducibility	• The decrease of bioluminescence was occurred due to any toxic compounds and no data available to demonstrate the specificity of detection towards PAHs	• Suggested to use as a biosensor for monitoring soil samples (Gu and Chang, 2001a)
Recombinant bioluminescent *E. coli*, GC2 (lac::luxCDABE)	Phenanthrene	Minimal detectable limit was 30 mg kg^{-1}	• The sensitivity of detection was improved using small sized glass beads during the development of sensing platform • Method was suitable to determine phenanthrene in industrial soil samples since the reported phenanthrene amount in the industrial samples are about six times higher than the minimal detectable limit by this sensor	• Method was not highly specific towards PAHs sensing	• Suitable for monitoring industrial soil samples (Chang et al., 2004)
Recombinant *E. coli* harbouring *pLZNRSAL*	Specific towards naphthalene and salicylate	LoD of 0.5 μM (0.069 ppm) and linear range of 0.5–10 μM towards salicylate sensing	• Simple and convenient method for monitoring PAH which present in gas and aqueous phase • High accuracy and reproducibility when tested across six consecutive tests • Generation of colorimetric signal which could identify using naked eye • Ability to test the real-time samples without any pre-treatment	• The LoD of the sensor was less sensitive than previous reported optical based method for salicylate sensing • The response from naphthalene was significantly greater in gaseous environment	• The system showed accurate and reliable results when tested the spiked waste water and gaseous samples (Cho et al., 2014)
DNA biosensors					
DNA	Three- to five-ring PAHs	0–10 mg L^{-1} detection range for both naphthalene and phenanthrene	• The ability to use this array-based approach for simultaneous detection of at least 50 samples • The real-time detection of PAHs in serum samples increased the sensitivity of detection towards high molecular weight PAHs	The use of carcinogenic (ethidium bromide) and harmful compounds to environment	• Assessed the spiked PAHs present in water and foetal calf serum samples (Doong et al., 2005)

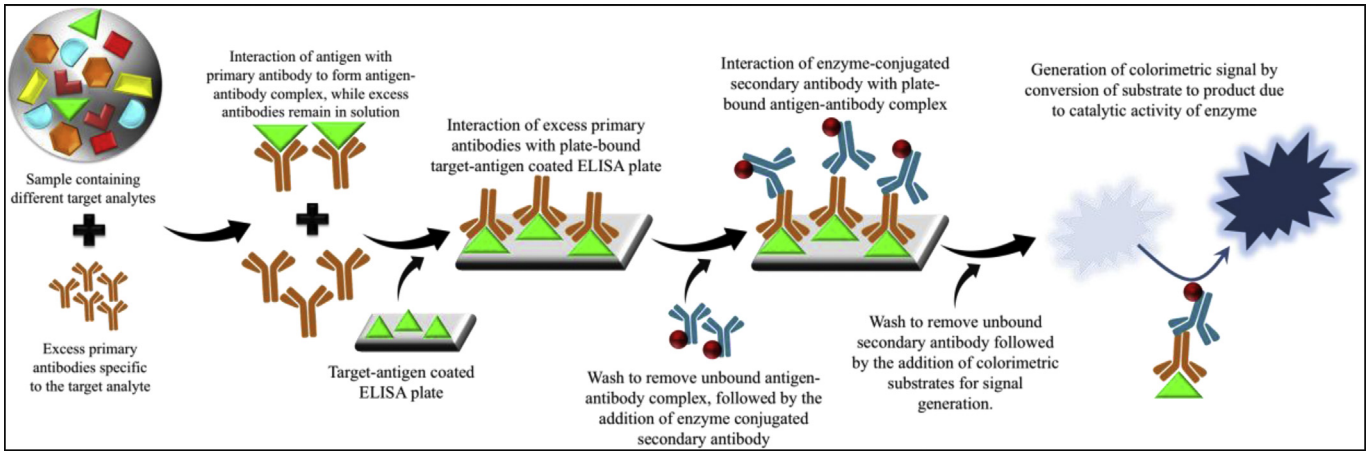

Fig. 4. Schematic representation of a competitive enzyme-linked immunosorbent assay.

exposed to PAHs (phenanthrene and pyrene) (Fillmann et al., 2002). This study suggested that urine samples offered a better option to quantify PAHs in crabs, as they provided higher accuracy in comparison to the haemolymph samples. Further, a distinctive difference was noted in the amount of PAHs determined in crabs collected from clean *vs.* contaminated sites. The good corroboration of kit-based results with UV-fluorescence spectrophotometry further validated the suitability of this competitive ELISA method for identifying PAHs in animals exposed to the PAHs containing environments (Fillmann et al., 2002). In another study, a commercially available RaPID-ELISA kit with some modifications was used for monitoring PAHs concentration in oiled guillemots in U.K. shores (Troisi and Borjesson, 2005). The main reasons for the modification of this kit include low-throughput (limited number of sample testing), requirement of magnetic tube rack, minimum sample volume (approximately 200 μl) and the recommended usage of the kit (testing abiotic samples). The modified method allowed highly sensitive detection of PAHs with as low as 0.2 ppb in the plasma of oiled seabirds, along with desirable characteristics, such as high-throughput, low-cost, simplicity, fastness in response and non-destructiveness. This highlights the relevance of using such strategies as a way to discover the internal PAHs concentration in seabirds during oil spillage and rehabilitation (Troisi and Borjesson, 2005).

While immunoassays seem to offer a number of advantages over conventional analytical techniques, as evident from the above discussed case-studies; the usage of these kits is not without certain shortcomings. For instance, the applicability of RaPID-ELISA kit was assessed for detecting PAHs present in river water samples (Barceló et al., 1998). The results revealed that the kit offered an excellent qualitative method for detecting PAHs without any false negatives. However, the comparison of quantitative results with gas chromatography coupled with mass spectrometry (GC-MS) showed that the kit had one order of magnitude higher readings, thereby recommending the suitability of this kit as a qualitative measure instead of a reliable quantitative technique (Barceló et al., 1998). Similar findings were noted during the assessment of an indirect ELISA method for detecting 1-nitropyrene with multidimensional HPLC (Zühlke et al., 1998). The comparison of the two aforementioned methods disclosed that immunoassay had six-fold higher readings, which were attributed to the presence of dinitropyrenes and other PAH species that could also potentially cross-react with the antibodies used in the assay (Zühlke et al., 1998). Notably, antibodies utilized in this immunoassay were designed to recognise the nitro group in the analyte and hence compounds with similar structural profile may lead to false positives. These studies highlight the prerequisite for a clean-up process to remove potential interference compounds from the sample while using these antibody-based immunoassays. These observations also question the real applicability of existing antibodies-based immunoassays for determining PAH concentrations in complex environmental samples that are likely to contain a variety of PAH species. The authors' argument is supported by another study which hypothesized that the overestimation of PAHs through immunoassays could be due to the presence of alkylated PAHs that are not accounted for, while using conventional methods such as GC-MS and HPLC. To validate this hypothesis, they conducted a comparative study that evaluated the accuracy of detecting PAHs using immunoassays and GC-MS, while considering the presence of total PAHs (unsubstituted and alkylated homologues of PAHs). The results showed that the estimation of total PAHs is a more viable and reliable measure for efficient evaluation of PAH concentrations *via* immunoassays (Spier et al., 2011).

In addition to the overestimation of PAH concentrations, cross-reactivity is another issue typically faced by immunoassays, as the antibodies used in these assays are generated against a group of PAHs with inherently similar structural profile. However, the cross-reactivity in these assays was also utilized as an advantage to detect PAHs just below the detection limit obtained from the conventional methods (Spier et al., 2011). For example, if the detection limit for GC-MS is 0.01 μg mL^{-1}, the concentration of PAHs below this value is not quantifiable by GC-MS. In contrast, the cross-reactivity of immunoassays allows producing a positive result as a summation of the interactions between all possible PAHs that can potentially interact with the antibody. As a result, it was claimed that the cross-reactivity in immunoassays may assist in minimising false positives during PAHs detection (Spier et al., 2011). In order to reduce the cross-reactivity in immunoassays during PAHs detection, a number of studies have also demonstrated the role of the utilized antibody (Matschulat et al., 2005). Antibodies generally used in these immunoassays are polyclonal antibodies, which consist of proteins or protein fragments that non-selectively interact with the analytes of inherently similar structure. As a result, these antibodies show broad affinity towards a group of structurally similar compounds. This cross-reactivity issue was minimised to certain extent by isolating monoclonal antibodies that showed higher specificities towards individual chemical compounds. The development of monoclonal antibody was reported against benzo[*a*]pyrene, leading to the generation of 14 different antibodies (Matschulat et al., 2005). The results showed that the purified monoclonal antibody from the clone 22F12 was able to detect benzo[*a*]pyrene effectively. The specificity study further revealed that the use of this antibody

resulted in less than 20% cross reactivity in the presence of other 16 PAHs identified by EPA, except for chrysene, indeno[*1,2,3-c,d*]pyrene and benzo[*b*]fluoranthene. This antibody reported minimal interference under different environmental parameters namely pH, ionic strength and inorganic ions and thus highlighted the appropriateness of using monoclonal antibodies towards highly specific detection of benzo[*a*]pyrene in drinking water (Matschulat et al., 2005). Another study described the use of highly specific monoclonal antibodies as a way to improve the sensitivity in these immunoassays (Li et al., 2016). The results revealed that the 2G8 clone had high affinity not only towards unsubstituted PAHs but also their common methylated PAH analogues, consisting of 3–5 rings. The comparison of the identified antibody with commercially available monoclonal antibodies for PAHs, namely 10C10 and 4D5, showed that the sensitivity of 2G8 was comparable to the commercial products. In addition to sensitivity, high specificity and superior IC50 value (concentration of the inhibitor required to reduce the maximum normalized response by 50%) were obtained supporting the applicability of 2G8 antibody for the recognition of PAHs with 3–5 ring structure. The fabricated biosensor using 2G8 antibody resulted in comparable results to GC-MS for a wide-range of environmental samples including water-soluble fractions from oil and creosote, to the sediment pore waters (Li et al., 2016). Overall, irrespective of the low specificity of these immunoassays; the cost-effectiveness, simplicity, rapid response and scalability has seen their on-going use for the identification of various PAHs, including 1-nitropyrene, the most abundant nitro-PAH in the environment with adverse mutagenic and carcinogenic effects (Zühlke et al., 1998).

5.2. Electrochemical biosensors for PAH detection

In addition to immunoassays-based PAHs detection, peroxidase substrate 3,3′,5,5′-tetramethylbenzidine (TMB) and hydrogen peroxidase (H_2O_2) have also been utilized to develop enzyme-coupled electrochemical immunosensors (Lin et al., 2007). The peak arising due to TMB oxidation occurring as a result of the catalytic activity of horseradish peroxidase (HRP) enzyme could generate a voltammetric signal that was exploited for the quantitative determination of PAHs. This electrochemical immunosensor could detect PAH concentrations as low as 0.02 ppb and the LoD was found to be 40 fold higher than that achieved by commercial RaPID assay kit. Further, the testing of PAHs in spiked tap water samples showed good sensitivity, suggesting the potential applicability of this method for testing PAHs in decentralized environmental samples (Lin et al., 2007). A similar electrochemical immunosensor, where TMB was replaced by hydroquinone as the substrate was also reported (Lin et al., 2012). The intra- and inter-batch reproducibility as well as the stability of the developed sensor further outlined the potential of this electrochemical immunosensor for monitoring PAHs in environmental samples (Lin et al., 2012).

Electrochemical sensing approaches for the determination of PAHs have been further extended to disposable screen-printed carbon electrodes (Fahnrich et al., 2003). The amperometric sensing in this case was achieved by utilizing a secondary antibody coupled with alkaline phosphatase (AP) enzyme. This enzyme specifically converts p-aminophenyl phosphate (*p*-APP) into p-aminophenol (*p*-AP), generating an amperometric signal. The study showed that the anthracene and chrysene PAHs had the highest cross-reactivity while minimal cross-reactivity was observed in the presence of acenaphthylene, benzo[*g,h,i*]perylene and dibenzo[*a,h*]anthracenes. An interesting feature in this study was the use of three independent approaches for the determination of phenanthrene; *viz.* co-exposure competition, indirect competition and indirect displacement for the determination of phenanthrene. Of the three approaches, the high sensitivity and reduced analysis time of the co-exposure competition assay suggested its suitability for amperometric immunosensor development. The analysis of spiked PAHs in tap and river water samples showed minimal changes in comparison to the original samples, suggesting the suitability of this approach for monitoring PAHs concentration in complex water samples (Fahnrich et al., 2003). Further the use of disposal screen-printed electrodes highlights the potential of conductometric sensing approaches for developing smart portable devices that may enable in-field identification/quantification of PAHs (Fahnrich et al., 2003).

5.3. Surface plasmon resonance (SPR) biosensors for PAH detection

The use of surface plasmon resonance (SPR) biosensor for detection of PAHs, such as benzo[*a*]pyrene, has also been explored (Miura et al., 2002). Benzo[*a*]pyrene is considered an ubiquitous PAH, and its presence in the environment is considered as an indicator to identify PAHs-contaminated sites. During the sensor fabrication, benzo[*a*]pyrene was first conjugated to bovine serum albumin (BSA), and this conjugate was then immobilized to the gold surface of the SPR sensor chip. The exposure of a benzo[*a*]pyrene-specific monoclonal antibody to this SPR chip resulted in competitive antigen-antibody interaction, causing a rapid change in the SPR angle. This change in the SPR angle was found proportional to the benzo[*a*]pyrene concentration, thereby allowing the quantitative estimation of benzo[*a*]pyrene in the detection range of 0.1–300 ppb (Miura et al., 2002). The same research group subsequently applied a similar approach for the detection of 2-hydroxybiphenyl (Gobi et al., 2003). In a subsequent study, the authors showed the ability of simultaneous detection of benzo[*a*]pyrene (10 ppt - 300 ppb) and 2-hydroxybiphenyl (10 ppt - 1000 ppb), suggesting the multiplexing opportunities offered by the SPR sensors (Gobi and Miura, 2004). The use of a similar approach for simultaneous detection of four endocrine-disrupting chemicals including benzo[*a*]pyrene, atrazine, 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-nonylphenol, was also demonstrated (Dostálek et al., 2007). This multichannel SPR sensor could detect these compounds with LoDs of 0.05, 0.07, 0.16 and 0.26 ng mL^{-1}, respectively. As such, these LoDs are within the maximum permissible limits set by regulatory bodies in the USA and EU for drinking water (Dostálek et al., 2007).

5.4. Fluorescence polarization immunoassays (FPIA) for PAH detection

Fluorescence polarization immunoassay (FPIA) is another technique that has been utilized for the determination of PAHs in the environment. The principle behind this approach is based on the difference in the optical rotation patterns inherent to the fluorescent dye (tracer) and the fluorescent dye molecule attached to an antigen or antibody, under a plane-polarised light. In general, the fluorescence dye is excited by plane-polarised light and emission takes place in the same plane-polarised plane. However, a rotation or tumble of the molecule during the excited state causes a shift in the plane-polarised plane and is considered as the depolarization of the emitted light (Nielsen et al., 2000). Based on this concept, the unbound tracer results in minimal or no polarization, whereas the bound tracer leads to increased polarization as a function of antigen concentration. The use of this approach for quantifying different PAHs, such as benzo[*a*]pyrene, naphthalene and anthracene has been reported with the LoDs of 0.9, 1.1, and 3.4 ng mL^{-1}, respectively (Yu Goryacheva et al., 2007).

5.5. Whole cell bacterial biosensors for PAH detection

The use of bioluminescent bacteria as biosensors for detection of PAHs has also been explored (Doong et al., 2005; Gu and Chang, 2001b; Lee et al., 2003). The first soil PAH biosensor in this category was developed based on a recombinant bioluminescent bacterium, *Escherichia coli* GC2 (*lac::luxCDABE*) and a non-toxic rhamnolipid biosurfactant. By coupling these two elements, a soil biosensor was constructed that could detect phenanthrene. The biosensing concept was based on the inhibition of characteristic bioluminescence in *E. coli* due to the toxicity of phenanthrene. The use of rhamnolipids facilitated the extraction of phenanthrene from soil, as PAHs show limited bioavailability in soil due to their hydrophobic nature. The rapid response time and reproducibility of the sensor performance suggested the ability to use bacterial bioluminescence as a new strategy for determining PAHs concentrations in soil samples (Gu and Chang, 2001b). In a subsequent study, the same research group employed glass beads for PAHs detection and investigated the relationship between the sensitivity of PAHs detection and the size of the used glass beads (Chang et al., 2004). This study showed that the use of different sizes of glass beads can modulate the performance of the bacterial biosensor, such that the sensitivity of phenanthrene detection could be improved by two folds (Chang et al., 2004). This was attributed to the transportation of a large number of phenanthrene micelles into the bacteria as a result of greater porosity obtained through the use of beads, which eventually resulted in significant reduction in the bioluminescence. Another independent study also evaluated the effect of the structure of PAHs towards the inhibition of bacterial bioluminescence. The results demonstrated that catacondensed PAHs, which are essentially PAHs consisting of no more than two rings in a single carbon atom, showed a dose-dependent bacterial toxicity, whereas minimal or no toxicity was observed in the presence of pericondensed PAHs (Lee et al., 2003).

Another study reported that luciferase-based bioluminescent sensors are fairly unstable, and may produce false positives and false negatives due to the existence of contaminants that can enhance or reduce the original bioluminescence signal. With these premise, the authors developed a recombinant *E. coli* system that could produce red colour in the presence of PAHs (Cho et al., 2014). The model PAHs that they investigated in this study included naphthalene and salicylate, a metabolite of naphthalene. The recombinant *E. coli* carried the *nahR::lac Z* fusion gene, wherein the *nahR* gene encoded for the *NahR* regulatory protein for naphthalene degradation and the lac Z gene encoded for the β-D-galactosidase enzyme. This recombinant *E. coli* in the presence of chlorophenol red-β-D-galactopyranoside substrate of the β-D-galactosidase enzyme could then produce a red colour in the presence of naphthalene that was detectable with the naked eye. The biosensor was able to selectively detect naphthalene and salicylate in comparison to the other tested PAHs. Further, the response against salicylate was much higher than the naphthalene, which was attributed to the low solubility of naphthalene in aqueous environment or higher sensitivity of the salicylate promote gene *Psal* over the naphthalene promote *Pnah* (Cho et al., 2014).

5.6. Fluorescence-based biosensors for PAH detection

The development of a sol–gel-derived array-based fluorescent DNA biosensor for simultaneous detection of multiple PAHs has also been reported (Doong et al., 2005). This sensor utilized the ability of PAHs to act as competitive DNA intercalators over standard intercalating dyes such as fluorescein isothiocyanate (FITC) and ethidium bromide (EDB). The working principle involved loading the dye-intercalated DNA in the sol-gel colloid and exposing these arrays to PAH-contaminated samples. Due to higher competitive DNA intercalating ability of PAH, they were then able to displace the fluorescent dyes that could be detected. The study involved assessing the ability of this strategy for the detection of different PAHs, including naphthalene, phenanthrene, fluoranthene and benzo[*a*]pyrene. The introduction of low molecular weight PAHs (naphthalene and phenanthrene) showed a concentration dependent (0–10 mg L^{-1}) decrease in the fluorescence intensity. However, a narrow detection range was observed in the presence of fluoranthene (0–3 μg L^{-1}) and no change in the fluorescence signal was observed in the presence of benzo[*a*]pyrene. The authors attributed this behaviour to the molecular weight of the utilized PAHs and supported this observation from their previous study where they noted a decrease in bioluminescence occurs only in the presence of low molecular weight PAHs (Lee et al., 2003). The authors claimed that the sol-gel fluorescence method was suitable for monitoring low molecular weight PAHs while also estimating PAHs in serum samples. Interestingly, the detection of PAHs in serum samples showed different trend to that observed in aqueous samples. This was attributed to the existence of dissolved organic components in serum samples which might have changed the relative solubility of different PAHs. For instance, the higher molecular weight PAHs such as benzo[*a*]pyrene can potentially accumulate more in serum samples than low molecular weight PAHs (Doong et al., 2005).

6. Bioremediation strategies for PAHs management

Considering the extremely high toxicity of PAHs across the entire ecosystem, there is an urgent need for sustainable solutions to accelerate the removal of PAHs. In specific context of the aquatic ecosystem, if the on-going accumulation of PAHs in aquatic resources is not timely managed, these highly persistent chemicals will gradually destroy the natural aquatic plankton and fish biodiversity. This will ultimately impact upon the livelihood and nutritional requirements of the human population. A number of promising technologies have been identified for remediation of PAH-contaminated environments. These have been reviewed elsewhere, and include soil washing, surfactant flushing, incineration, thermal desorption, landfarming, soil vapor extraction, excavation and landfilling, bioremediation, and other emerging technologies (Kuppusamy et al., 2017). However, in the context of inland aquatic ecosystems, most of these technologies will face practical challenges for implementation. The authors believe that bioremediation may offer a promising, low-cost, sustainable and effective PAHs removal strategy in inland aquatic ecosystems without significantly disturbing the natural environment. Therefore, the current review has only focussed on potential bioremediation strategies for PAH removal. Further, considering the biosensor technologies available for PAH detection have not been reviewed elsewhere so far, to keep the review focussed, only the key aspects of bioremediation have been discussed here, while further details are included in the **supplementary information** (Figs. S1–S6 and Table S1).

As such, bioremediation is a process that involves transformation of harmful organic compounds into less harmful or harmless entities by utilizing the metabolic ability of microorganism (Margesin et al., 2000). The main philosophy behind bioremediation is the acceleration of the biodegradation process by providing the optimum condition for microbial growth with a preference to use PAH as a feedstock for their metabolic activities (McFarland et al., 1996). To this end, a number of microorganisms, including bacteria and fungi, that have the ability to degrade a variety of PAHs have been isolated and characterized (Table S1). The current review only provides a brief overview of selected

bioremediation strategies for PAHs to represent their future potential, and the readers are directed to read focussed reviews on PAHs bioremediation for a deeper understanding of this subject (Bamforth and Singleton, 2005; Mrozik et al., 2003; Wilson and Jones, 1993). It is also noted that in the current review, bioremediation strategies are discussed only for six out of 16 most-studied PAHs (as elaborated below), while readers are directed for additional studies for bioremediation of other 10 PAHs, including acenaphthylene (Poonthrigpun et al., 2006), acenaphthene (Mihelcic and Luthy, 1988), fluoranthene (Gordon and Dobson, 2001), benzo[*a*]anthracene (Moody et al., 2005), chrysene (Dhote et al., 2010), benzo(*b*)fluoranthene (Tersagh et al., 2016), benzo(*k*)fluoranthene (Preuβ et al., 1997), dibenz[*a,h*]anthracene (Juhasz et al., 1997), benzo[*g,h,i*]perylene (Xia et al., 2006), and indeno[*1,2,3-c,d*]pyrene (Straube et al., 2003).

6.1. Biodegradation of naphthalene

Naphthalene is an important PAH with a fused pair of benzene rings. According to International Agency for Research on Cancer (IARC) of the WHO, naphthalene is considered as a possible human carcinogen. Although naphthalene is considered moderately toxic to several species of fish, water fleas, Pacific oysters, and the green algae (EPA, 2008), it has been among the most-studied PAH for biodegradation studies. This is due to its reasonable aqueous solubility which reduces the complexity of performing experiments. A number of bacteria belonging to the genera *Mycobacterium, Cyanobacterium, Bacillus, Aeromonas, Pseudomonas, Sphingomonas, Burkholderia, Ralstonia, Polaromonas* and *Enterobacter* species have been noted for their capacity to degrade naphthalene (Table S1). In particular, a metabolically versatile *Rhodococcus* strain was able to grow on naphthalene as its sole carbon and energy source (Tomás-Gallardo et al., 2014). In another study, a *Pseudomonas* strain isolated from soil sediments of municipal wastes was able to degrade a variety of PAHs, including naphthalene, phenanthrene, fluoranthene and anthracene (Mukesh Kumar et al., 2012). The typical microbial pathway involved in naphthalene degradation is outlined in Fig. S1.

6.2. Biodegradation of fluorene

Fluorene, one of the most important components of fossil fuels and coal derivatives, consists of two benzene rings coupled with a pentagonal ring (cyclopentane ring) and is listed as a priority pollutant by the EPA (Gomes et al., 2006). A number of bacteria belonging to the genera *Brevibacterium, Burkholderia, Mycobacterium, Arthrobacter, Pseudomonas, Sphingomonas, Micrococuss, Rhodococcus,* and *Staphylococcus* have been reported for their ability to degrade fluorene through using it as their sole source of carbon (Table S1). In addition to bacteria, the white-rot fungus *Pleurotus eryngii* F032 has also been observed to show fluorene degradation capability (Hadibarata and Kristanti, 2014). Structurally, fluorene is susceptible to aerobic oxidation at three different positions. Firstly, a naphthalene-like oxidation to one of the aromatic ring generating dihydrodiol, secondly oxidation of the carbon atom adjacent to the methylene group of fluorene, and thirdly oxidation of the methylene group (Bressler and Fedorak, 2000). The first two processes involves dioxygenation, however the third process is initiated by monooxygenation at C-9 (Sokolovska et al., 2002). The catabolic pathway for fluorene degradation by *Sphingomonas* sp. that involves monooxygenation at C-9 is outlined in Fig. S2. Crude oil wells (Yu et al., 2014) and municipal sludge (Othman et al., 2011) have been reported as a potential source of fluorene degrading bacteria, offering opportunities for isolating PAH-degrading microorganisms from exotic environments.

6.3. Biodegradation of phenanthrene

Phenanthrene consists of three fused benzene rings, where the name phenanthrene is derived from a composite of phenyl and anthracene. It is found in cigarette smoke in its pure form, and is a known irritant and photosensitizer. A variety of bacterial strains belonging to the genera *Arthrobacter, Acidovorax, Burkholderia, Brevibacterium, Sphingomonas, Pseudomonas, Aeromonas* and *Mycobacterium* have been reported to have the capacity to utilize phenanthrene as the sole carbon and energy source (Table S1). Comparison of the metabolic pathways for phenanthrene degradation by *Brevibacterium* sp. and *Pseudomonas* sp. has revealed that different microorganisms may involve remarkably different mechanisms for PAH degradation (Fig. S3). An interesting study showed that the inoculation of plants with an endophytic *Pseudomonas* strain isolated from clover (*Trifolium pratense* L.) grown in a PAHs contaminated site, could reduce the risks associated with plant contamination by phenanthrene (Sun et al., 2014). Such studies point towards importance of PAH-resistant (catabolically active) genes activated in both lower and higher forms of organisms over period of long exposures to PAH contaminated sites, and future potential of exploring these natural selection processes for efficient PAH bioremediation.

6.4. Biodegradation of anthracene

Anthracene is another widely distributed PAH consisting of three fused benzene rings and used for the production of a variety of products such as dyes, plastics, pesticides, smoke screens and scintillation counters. Anthracene can enter into lungs through breathing contaminated air, causing respiratory and pulmonary diseases, as well as through skin contact with contaminated soil or products such as, coal tar, roofing tar, heavy oils or the sites where PAHs are common. Grilling and charring the food also increases the amount of anthracene present in the food. Microorganisms belonging to the genera *Pseudomonas, Sphingomonas, Nocardia, Mycobacterium, Rhodococcus, Corynebacterium* and *Streptomyces* have been observed to be able to mineralize anthracene (Table S1). The anthracene degradation pathway by a *Mycobacterium* strain is outlined in Fig. S4.

6.5. Biodegradation of pyrene

Pyrene, consisting of four fused benzene ring, is the smallest peri-fused PAH. While pyrene is not considered carcinogenic, it instead causes toxicity to kidneys and liver. Due to its high thermal stability, pyrene is produced in a wide range of combustion conditions, and is a common by-product of combustion processes. Pyrene can persist in environment for long durations depending on the environmental conditions, and is found to be toxic to aquatic micro-invertebrates, in which it is transformed into highly toxic quinone that has high mutagenicity (Belkin et al., 1994; Bolton et al., 2000). A number of bacterial degradation pathways involving *Mycobacterium, Sphingopyxis, Sphingomonas* and *Pseudomonas* species (Table S1) has been reported for pyrene, among which, the genus of *Mycobacterium* has been extensively reported for degradation of pyrene (Fig. S5). Another notable observation about bioremediation of pyrene is that pyrene degradation ability remarkably varies from species to species within the same genera (Shokrollahzadeh et al., 2012). This suggests that highly targeted bioremediation approaches may be required for efficient degradation of pyrene in the environment.

6.6. Biodegradation of benzo[a]pyrene

Benzo[*a*]pyrene is a ubiquitous five aromatic ring PAH produced as a result of incomplete combustion of organic matter. It is considered as a priority pollutant because of its carcinogenic, teratogenic and mutagenic effects (Bhattacharya et al., 2014). Benzo [*a*]pyrene has a high octanol/water partition coefficient ($LogK_{o/w}$ − 6.06) and low water solubility (0.0023 mg L^{-1}), which makes it particularly resistant towards microbial degradation (Seo et al., 2009). A number of bacterial species ranging from *Bacillus, Mycobacterium, Sphingomonas, Stenotrophomonas,* and *Micrococcus* (Table S1) have been noted for their benzo[*a*]pyrene degradation capacities, albeit with varying efficiencies. Fig. S6 depicts the catabolic pathway involved in the degradation of benzo[*a*]pyrene by *Mycobacterium* species. In addition to bacteria, filamentous fungi including *Aspergillus flavus, Cladosporium cladosporioides, Gliocladium viride, Paecilomyces farinosus* and *Talaromyces rotundus*, as well as the white-rot fungus *Pleurotus ostreatus* have also been reported with benzo[*a*]pyrene degrading capacity (Table S1).

7. Summary and future outlook

PAHs are important environmental contaminants originating from natural processes as well as anthropogenic activities. These highly persistent organic molecules of high hydrophobicity are extremely toxic to planktons and fishes, hampering their biodiversity in natural aquatic resources. A number of PAHs-induced harmful effects including growth reduction, enzymatic disorder and photosynthesis inhibition have been established in planktons. Similarly, a number of disorders including the inhibition of acetylcholinesterase activity; endocrine disruption; increased lipid peroxidation, catalase activity and cytochrome P4501A1 expression; decreased ovarian somatic index, and reduction in egg counts are commonly observed in the fish biodiversity. To counter these harmful effects of PAHs, a number of strategies for PAHs remediation have emerged over the past century. However, in most of the cases, the remediation approaches fail at the field-scale due to several technical and non-technical factors (Kuppusamy et al., 2017), the most important being the associated cost and practical challenges in deploying them at large scales. Among these, the authors see bioremediation strategies occupying a niche space to denature PAHs within the natural ecosystems in a sustainable manner. During bioremediation, certain microorganisms are able to degrade a variety of PAHs through utilizing them as their carbon and energy source. However, the currently achieved biodegradation rates of PAHs are low due to the bioavailability limitation or membrane influx limitation posed by poor water-solubility of PAHs. There is a need to screen for more efficient PAHs degrading microorganism from natural ecosystems. Since a number of microbial species co-localized at a single site may synergistically contribute to PAH remediation, there is a need to undertake microbial fingerprinting using environmental metagenomics approaches to design more robust bioremediation strategies. Another possibility might be to employ genetic engineering approaches to enhance the biodegradation capabilities of microorganisms; however this approach may still face certain challenges for environmental bioremediation due to issues associated with environmental release of genetically-modified (GM) organisms. These GM microorganisms may however be suitable for batch purification of controlled aquifers during fish/seafood farming. This will also necessitate further developments to design suitable remediation reactors for removal of PAHs under anaerobic conditions, and in-parallel identification of anaerobic and facultative aerobic organisms that may offer new avenues for PAHs remediation. Due to the hydrophobic nature of PAHs, it is likely that anaerobes may outperform aerobic organisms in PAHs bioremediation. Further, emerging approaches such as nano-remediation and poly-hetero microbial remediation that have found applications in successful remediation of other organic pollutants might also be extended to PAHs remediation (Anderson et al., 2016; Kuppusamy et al., 2016a; Kuppusamy et al., 2016b; La et al., 2017; La et al., 2016; Mohammadtaheri et al., 2016; Pearson et al., 2011a; Pearson et al., 2011b; Pearson et al., 2011c; Pearson et al., 2012; Ramanathan and Bansal, 2015; Singh et al., 2018; Siu et al., 2017). An integrated approach combining bioremediation and nano-remediation may, in turn promote the expansion of 'green nano-biotechnology' approaches in sustainable environmental clean-up of PAHs (Sanyal et al., 2005).

Another important consideration for effective PAHs management is the development of new analytical tools and technologies for rapid, ultrasensitive, highly specific and low-cost detection of different PAHs. In the absence of reliable PAHs detection tools, the management of PAHs is going to face significant challenges. The current detection of PAHs still heavily relies on traditional analytical techniques that are time-consuming, expensive and lack high-throughput capacity. Although a variety of biosensing platforms have been investigated for PAHs detection, the poor selectivity towards specific PAH compounds has remained an on-going concern, requiring further improvements or development of transformational approaches for efficient, sensitive and selective PAH detection in real-world samples. This non-specificity issue arises due to the use of polyclonal antibodies as MREs in these sensors, and these antibodies tend to cross-interact with many different structurally-similar PAHs. The introduction of monoclonal antibodies has been able to overcome this limitation to a certain extent; however the currently-achieved specificity still remains far below desirable. Further, the high time-, cost-, and technical-intensiveness required for antibody production, and poor ambient stability of antibodies thrives for the discovery of alternative more promising MREs that could potentially replace antibodies with a much powerful performance. Aptamers is one such promising candidate that may have a significant role to play in the development of future PAH-based biosensors (Cho et al., 2009; Dhiman et al., 2017). Aptamers are short (typically 20-30mers) single standard DNA sequences which are generated through a process called "systematic evolution of ligands by exponential enrichment" (SELEX). The multiple selection rounds that take place during the selection of a target-specific aptamer allow aptamers to show ultra-high specificity towards the cognate target. In addition, the low cost of production, stability under elevated conditions and discovery of these target-specific MREs under *in vitro* conditions, without the requirement of animals highlights important benefits of developing PAHs-specific aptamers over antibodies. Another extraordinarily important feature of aptamers is that they can be generated against a vast range of targets, ranging from small molecules to larger biomolecules to even whole cells. Recent studies have discussed the development of aptamers against polychlorinated biphenyls (PCBs). These PCBs belong to the family of chlorinated hydrocarbons and similar to PAHs, they are organic environmental contaminants of high importance (Mehta et al., 2012). While aptamers against PAHs are currently not known, the possibilities of developing PAH-specific aptamers will offer immense opportunities in developing highly specific PAH sensors.

Overall, the authors believe that high eco-toxicity and environmental ubiquity of PAHs warrant consolidated efforts to address this global problem, before it becomes beyond manageable. Effective management of these concerning pollutants will require parallel research efforts towards developing efficient biosensors that can reliably detect PAHs, and therefore assist in their effective management through newly discovered bioremediation processes.

While nanotechnologies are already playing key roles in developing clinical biosensors and diagnostic devices, those platforms have not been actively utilized for environmental management (Holzinger et al., 2014; Li and Rotello, 2011; Sharma et al., 2015; Son et al., 2014; Vigneshvar et al., 2016; Weerathunge et al., 2016). Future deployment of nanotechnologies and other cross-disciplinary technologies for environmental detection and remediation of PAHs may offer a viable integrated solution to make the planet Earth cleaner and safer for future generations.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.05.016.

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