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Remediation approaches for polycyclic aromatic hydrocarbons (PAHs) contaminated soils: technological constraints, emerging trends and future directions

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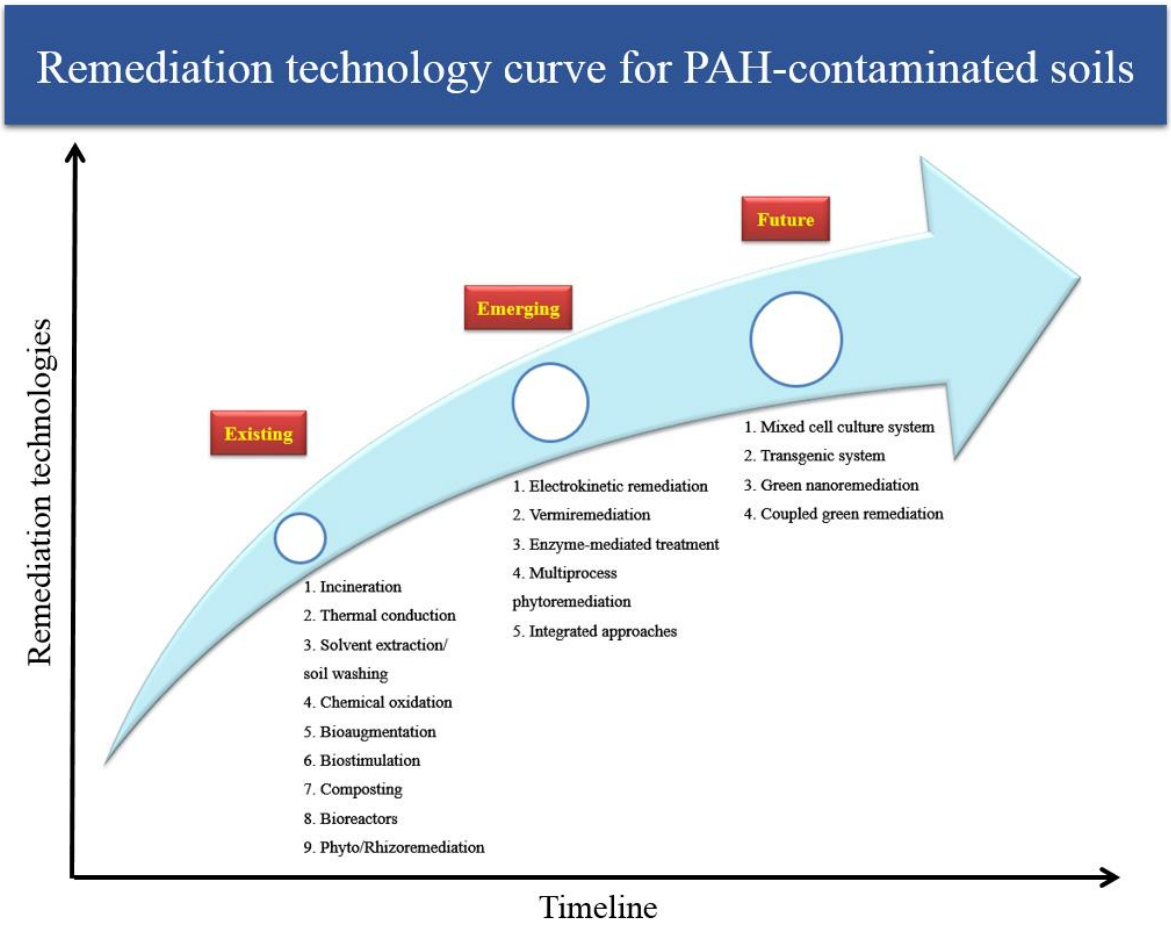
GRAPHICAL ABSTRACT



Abstract

For more than a decade, the primary focus of environmental experts has been to adopt risk-based management approaches to cleanup PAH polluted sites that pose potentially destructive ecological consequences. This focus had led to the development of several physical, chemical, thermal and biological technologies that are widely implementable. Established remedial options available for treating PAH contaminated soils are incineration, thermal conduction, solvent extraction/soil washing, chemical oxidation, bioaugmentation, biostimulation, phytoremediation, composting/biopiles and bioreactors. Integrating physico-chemical and biological technologies is also widely practiced for better cleanup of PAH contaminated soils. Electrokinetic remediation, vermiremediation and biocatalyst assisted remediation are still at the development stage. Though several treatment methods to remediate PAH polluted soils

currently exist, a comprehensive overview of all the available remediation technologies to date is necessary so that the right technology for field-level success is chosen. The objective of this review is to provide a critical overview in this respect, focusing only on the treatment options available for field soils and ignoring the spiked ones. The authors also propose the development of novel multifunctional green and sustainable systems like mixed cell culture system, biosurfactant flushing, transgenic approaches and nanoremediation in order to overcome the existing soil- contaminant- and microbial-associated technological limitations in tackling high molecular weight PAHs. The ultimate objective is to ensure the successful remediation of long-term PAH contaminated soils.

Keywords: PAHs, Long-term contaminated soils, Treatment technologies, Biodegradation, Field-scale remediation, Future strategies

1. Introduction

Of the 1,408 hazardous waste sites that are targeted for long-term federal cleanup by US EPA, at least 600 sites have been found to be contaminated with a most important class of organic contaminants, namely PAHs (Okere and Semple, 2011; Duan et al., 2013). PAHs are ubiquitous hazardous micropollutants and highly resistant to degradation, commonly being found at sites associated with petroleum, gas production and wood processing industries. PAHs represent a broad group of physico-chemically different individual molecules made of two or more unsubstituted benzene rings fused together when a pair of carbon atoms is shared between them (Mohan et al., 2006; Okere and Semple, 2011; Kuppusamy et al., 2016a). Several hundred different combinations of PAHs exist, but only about 28 compounds were labelled hazardous by US EPA in 2008 (Gan et al., 2009). The two main classes of PAHs are the LMW and HMW PAHs. The LMW PAHs (2 to 3 ring PAHs) such as naphthalene,

fluorene, phenanthrene and anthracene are shown to have significantly less toxicity compared to the HMW PAHs of 4 to 7 rings (from chrysene to coronenes) which are recalcitrant and carcinogenic to humans (Duan et al. 2013; Kuppusamy et al., 2016b).

PAHs are everywhere and their ultimate sink is the soil. In fact, globally 90% of the environmental PAH burden is present in soils (Wild and Jones, 1995). Remediation of PAH contaminated sites are of great importance owing to the risks posed by PAHs to receptors, need for the site and the extent of exposure and potential toxicity. Generally, contaminated soils are excavated, transported to new sites and accumulated as landfill. This practice is not a preferred approach as the threat is only transferred to future generations (Wise, 2000) without creating an ultimately secure remedy. For more than 20 years, significant research has been directed to removing or degrading PAHs from contaminated soils to their background levels. This had led to the outbreak of several physical, chemical and biological remediation approaches that can overcome the issues of PAH contaminated soils (Gan et al., 2009; Kuppusamy et al., 2016c). Irrespective of existing strategies used by stakeholders, remediation of PAH contaminated sites remains a great challenge due to soil heterogeneity. For instance, the rate of remediation could be either fast or slow depending on the soil types and related factors and at times ends up producing transformed compounds (oxygenated derivatives) that are more toxic than the original parent PAHs (Bandowe et al., 2016; Wang et al., 2016). Because of these constraints and a few others that are discussed briefly in the later part of the review, the need for emerging technologies is clearly evident. Furthermore, avenues have emerged for the design of new remediation strategies that can overcome existing technological limitations.

Many reviews had described the established remediation approaches that are suitable for PAH contaminated soils (Wilson and Jones, 1993; Wise, 2000; Samanta, 2002; Mohan et al., 2006; Rivas, 2006; Gan et al., 2009; Kuppusamy et al., 2016d; Kuppusamy et al., 2016e).

Of these the majority of studies had only provided a comprehensive overview of an individual or specific technology, or had considered the treatment of spiked soils instead and/or with real contaminated soils. So far systems that are proven to be successful with the use of spiked soils had failed to perform well in field soils because real contaminated soils are much more complex. Also a well-defined set of information on the existing and emerging technologies will act as a support system allowing users to make the right decision on the most suitable technique(s) adoptable for the site remediation or management. In this review, we critically evaluate and discuss the following: (i) extent and severity of global PAH pollution in soils; (ii) established remediation technologies for PAH contaminated field soils; (iii) emerging technologies for on-site PAH remediation; and (iv) current constraints as well as future prospects for developing innovative approaches to enhance the efficacy of PAH remediation at contaminated sites. Notably, as the theories behind individual remediation technologies are reported extensively in the specialized literature, we have focused mainly on highlighting the success and failures of those technologies in contaminated sites.

2. PAHs in soils

2.1. Sources of PAHs at contaminated land

The composition of PAH mixtures in soil are dominated by two major source patterns: natural PAHs and anthropogenic emissions. Global atmospherically transferable PAH emission sources are presented in Fig. 1 (calculated based on the reported PAHs emission activity by different sources for the reference year 2010) (Zhang and Tao, 2009). Locations that lie in close proximity to long-term emission sources receive high atmospheric depositional inputs/discharge from petroleum, gas-production or wood processing industries, transport activities and industrial effluents or through accidental spill of unburnt petroleum contribute to localized loading of PAHs in soil. The combustion-derived residues (pyrogenic)

contain a relatively large abundance of high molecular mass 4 to 6 ring PAHs (Essumang et al., 2011) due to the dominance of alkylated parent PAHs structures over petroleum-derived PAHs (petrogenic). For instance, sites where wood combustion, gasification/liquefication of fossil fuels, carbon-production and use has occurred are frequently contaminated with high concentrations of fluoranthene, pyrene, chrysene and benzo[a]pyrene. Since PAHs are the major constituents of creosote (85% PAHs by weight) (Wilson and Jones, 1993), industrial activity associated with coal tar/coal tar-pitch production and use results in the disposal of significant quantities of phenanthrene, fluoranthene and pyrene. Coke production is commonly associated with anthracene, phenanthrene and benzo[a]pyrene containing materials. Fluoranthene, pyrene, benzo[b]fluoranthene and benzo[k]fluoranthene contamination have been detected on sites where e-waste recycling (Zhang et al., 2012), catalytic crackling, fuel/oil storage, transportation, processing, use and disposal have occurred. Phenanthrene, fluoranthene, pyrene, chrysene and benzo[a]pyrene in the soils of many industrially contaminated sites are also derived from open burning of tyres/coal/refuse, incineration, asphalt production and use (Duan et al., 2013).

In the meanwhile, PAHs have been detected around the world even at sites which are far from industrial activity such as the tropics and the polar regions due to these chemicals' 'long-range atmospheric transport'. In many tropical soils, naphthalene, phenanthrene and perylene are most abundant and are present at higher concentrations than in temperate soils. In temperate soils, HMW compounds such as benzo[a]fluoranthene frequently dominate (Mohan et al., 2006). Thus sources of PAHs pollution are diverse and changes in emission source or transport pathways could influence the qualitative distribution profiles of PAHs. Attempts to identify the primary PAHs source in the field studies is a requisite to control the further soil contamination and several methods have been proposed to apportion these sources, most widely the diagnostic ratios (relative molecular concentration of PAHs are

considered to calculate the diagnostic ratios) (Tobiszewski and Namiesnik, 2012; Shi et al., 2014) as given in Table 1.

2.2. Concentration levels – industrial *vs* non-industrial sites

In general, soil PAH concentrations have increased over the last 30 years, especially in industrialized regions of the world and they will increase in the following 5 or more years due to ever-increasing anthropogenic emissions (Fig. 1). According to Malawska and Wiolkomirski (2001), a soil is regarded as unpolluted if the standard PAH content is <0.2-0.6 mg kg^{-1} PAHs. If the total PAHs contents range between 0.6-1, 1-5, 5-10 and >10 mg kg^{-1} then the soil is regarded as slightly polluted, polluted, heavily polluted and very heavily polluted, respectively. Depending on the source of contamination, soils can contain PAH concentration ranging between 0.001 to 300,000 mg kg^{-1} total PAHs (Kanaly and Harayama, 2000; Bamforth and Singleton, 2005). Wilcke (2007) reviewed the global pattern of PAHs in soil (0.004-186 mg kg^{-1}) and stated that Central Europe (Germany and Czech Republic) are more contaminated with PAHs than all other parts of the world studied such as China, Russia, Thailand, America, Brazil and Ghana. In yet another report by Loganathan et al. (2011), there were more PAHs in Indian soils compared to Africa, Iran, Brazil, Russia, Canada and Australian soils. Thus PAHs could be one of the universal pollutants with a high degree of variation in their concentration levels in different regions.

Reports have been published with specific reference to PAH concentration on contaminated land. Particularly, most of the abandoned industrial sites are not easily accessible to scientists due to legal and liability issues associated with transport and storage of the contaminated soils, hence still a large number of them are unexplored. Those available are summarized in Table 2. Notably, concentrations of all 28 priority PAHs listed by US EPA in soils are not available, which highlights that new research can and should focus on

investigating all priority PAHs in contaminated land, risks associated with contamination and determine the degree of remediation required. It should also be stressed that locations, sampling methods and analytical procedures vary at each site and the values in Table 2 are the concentration range of specific PAHs that aims to give an overall impression of the PAH profile on different sites.

Compilation of the data available between 1990 and 2014 (see Table 2), reveals that manufactured gas plant (MGP) sites are the foremost PAHs hotspots compared to all other industrial sites in the following order: MGP sites (~ 1841-16546 mg kg^{-1} total PAHs) > wood preserving and treatment sites (~ 15-12717 mg kg^{-1} total PAHs) > coking plant (~ 1406-8053 mg kg^{-1} total PAHs) > manufacturing zones (~ 7-14 mg kg^{-1} total PAHs) > petrochemical plants (~ 0.08-1 mg kg^{-1} total PAHs). Of the non-industrial regions, roadsides (~ 0.5-49 mg kg^{-1} total PAHs) constitute the majority of PAHs contamination over forest (~ 0.2-1 mg kg^{-1} total PAHs) and residential areas (~ 0.1-4 mg kg^{-1} total PAHs). Further, of the specific PAH compounds, HMW PAHs are found to represent the majority of PAHs contamination (80-90%) at evaluated sites globally. This clearly means that the remediation of PAH contaminated sites is difficult because of the dominance of distinct HMW PAH mixtures that are less bioavailable and also very much resistant to degradation. Consequently, there is significant pressure on researchers and stakeholders of contaminated lands to develop effective remediation approaches that can mitigate HMW PAHs at real field conditions.

2.3. Extent and status of global PAHs-contaminated sites – MGP sites

Most of the PAH contaminated abandoned industrial sites that were once located in the periphery of urban land have been pushed to the middle of cities due to enormous economic demand for commercial, recreational or residential areas created by rapid population growth, urbanization and suburban expansion (Thavamani et al., 2012). As a

result, currently many PAH contaminated sites lie on high value commercial land and remediation of such sites is a priority. Of all the PAH contaminated sites, due to high contamination levels (Table 2), rapid and continuous expansion of the contamination zone and difficulty in remediation caused primarily by occurrence of mixed contamination (example: presence of LMW and HMW PAHs mixtures with toxic heavy metals), sustainable and economic remediation of MGP sites remains a challenge for current and future research. For these reasons MGP sites are the focus.

It is estimated that currently more than 58,900 MGP and related coke-oven sites exist worldwide (Fig. 2a). Some developing countries such as China, India, Russia, etc. are not included in this enumeration due to the lack of information (Wehrer et al., 2011). Available MGP site remediation data for developed nations such as the US, Australia and New Zealand shows that nearly 5-30% of the identified MGP sites in individual nations have been investigated at field-scale. Indeed, of the 36,000-55,000 MGP sites located in the US (Marilyn, 2011), only 200-300 have been remediated. In the case of Australia and New Zealand, 20 and 2 out of 132 and 51 sites are only remediated (Thomas and Hosking, 1995), respectively (Fig. 2b). It is important to understand that not all of the identified sites require cleaning up. However, it is necessary to carefully investigate each MGP plant and confirm if it requires remediation or not. In this view, globally more than 90% of identified MGP sites in developed countries are yet to be investigated, characterized and remediated. In the developing nations such sites are yet to be identified.

2.4. Fate of PAHs in soils

To remediate a PAHs contaminated soil, it is important to understand its fate in this scenario. Although the fate of PAHs in soils has been well reviewed (Wilson and Jones, 1995; Okere and Semple, 2011; Duan et al., 2013), the following section here emphasizes the

main processes that determine the behavior – loss or removal of PAHs in the soil. Fig. 3 is a conceptual model depicting the fate of PAHs in soil over time. PAHs that enter soil may be lost or degraded by a number of physico-chemical and biological processes such as volatilization and/or photo-oxidation to the atmosphere, irreversible sorption to soil organic matter, leaching to groundwater, abiotic loss (influence of daily seasonal temperature fluctuation), uptake by plants or microbial degradation (Okere and Semple, 2011). The rate at which these processes occur and the degree to which PAHs are degraded or retained within the soil is controlled by a number of factors including: (a) soil properties – soil type (organic matter, clay or mineral content, structure and composition of humic material), soil temperature, moisture, redox potential, nutrient availability, presence and activity of degrading microorganisms; and (b) physico-chemical properties of the individual PAHs – molecular mass, bioavailability, toxicity and biodegradation half-lives (Wilson and Jones, 1993; Duan et al., 2013). For instance, LMW PAHs when they enter soil are lost rapidly and become more mobile and degradable (low Kow value, high water solubility and volatility). On the other hand HMW PAHs are more persistent and resistant to degradation. Most PAH compounds show biphasic behavior where though losses occur, the rate and extent of these losses decrease as time passes due to the decrease in bioavailable PAH fractions. For example, this applies to soils with high organic matter and clay content where PAHs are protected by their binding/sequestration to organic matter and diffusion into micropores, thus limiting their degradation (Okere and Semple, 2011). The major means by which PAHs are lost from soils is biotic, i.e. through degradation or co-degradation processes mediated by bacteria, fungi or algae. Bioavailability of the sorbed contaminants to microorganisms is crucial to the biodegradation of PAHs in soil (Juhasz and Naidu, 2000; Stroud et al., 2007; Okere and Semple, 2011; Cebron et al., 2013).

Notably, adsorption and sequestration are the two main processes that control PAHs release into the soil solution, thereby limiting their bioavailability (Barnier et al., 2014). PAHs bioavailability in soil is also strongly reduced by aging and the high levels of PAHs found in the old brownfield sites may not be a real threat due to their poor bioavailability (Ouvrard et al., 2013). For instance Ma et al. (2012) witnessed a decrease in the bioavailability of PAHs in soils which was consistent with the uptake rate and the bioconcentration factor of earthworms as aging time prolonged.

3. Assessment and remediation of PAHs-contaminated land – a phase approach

A typical contaminated site remediation scheme involves three phases: (I) site reconnaissance and risk assessment, (II) remedial options appraisal, and (III) remediation and monitoring (Ashraf et al., 2014). Phase I aims to investigate if the land has been contaminated with PAHs or not (site characterization and preliminary risk assessment) and if the concentration of PAHs exceeds that set out in the available local or national guidelines (Table 3) and land end-use. Following this the site is declared to be polluted and requires the implementation of a soil management program. The management program first addresses source control to stop on-going PAH releases. After understanding the extent of contamination, remediation objectives are developed in a variety of ways ranging from generic national guidelines to site-specific risk assessment (human, ecological and environmental). Briefly a site-specific risk assessment is as follows: firstly, problem formulation (PAH distribution and concentration in relation to the receptors and their patterns of activity on the site); secondly, exposure assessment (pathway by which PAHs are taken up by the receptors); thirdly, toxicity assessment (adverse effects that PAHs pose to receptors and the dose at which these effects occur); and fourthly, ending with risk characterization (comparing the data obtained from exposure assessment, in other words uptake rate and

toxicity assessment, i.e. toxic dose and determine whether or not an adverse effect is likely to occur). Risk assessment procedures can also be used to back calculate PAH concentration in soil at which no adverse effects are expected.

Phase II involves identification, detailed evaluation of feasible remedial options and development of remediation strategies. Generally before implementing a technology at field-scale, efficacy of the selected remedial options is predicted by feasibility and treatability studies in the laboratory and/or on-site (microcosm PAH degradation test using historically contaminated soils, liquid-culture batch or column experiments). Determining the quantity of PAHs that are desorbable from the soil matrix, degradation rate, microbial enumeration of PAHs degraders, bioluminescence-based biosensor assay, dehydrogenase activity, soil respirometric tests, ecological impact and toxicity assessment, microbial survival test and tracking of inoculated organisms can be used for the feasibility or treatability assessment of soil remediation (Balba et al., 1998; Diplock et al., 2009). The results of feasibility and treatability studies obtained in phase II are used to define the most appropriate remedial action for a particular contaminated site. In phase III, implementation of suitable remediation strategies is carried out where the remediation technology is put into action and long-term monitoring and maintenance are implemented. Ecological and health risk assessments are once again executed to confirm if risk-based remediation of contaminated land (Duan et al., 2013) is achieved or otherwise by the adopted remediation strategy. If risk persists, then the site has to be subjected to further remediation.

4. US EPA's options for the remediation of PAHs-contaminated sites and costs

Until the late 1990s, excavation and landfilling had been done at a majority of PAH contaminated MGP sites worldwide that required remedial activities. However, in 2000, the promulgation of land disposal restrictions (LDRs), maximum landfill levy, higher operation

and maintenance costs have made public utilities rethink and adopt the comparatively cost-effective in-situ cleanup treatments. The current in-situ remediation alternatives used at MGP sites by US EPA include soil vapor extraction, bioremediation, thermal desorption, incineration, surfactant flushing and soil washing. For any site cleanup, costs have played an important role in the selection of site remedial options (Kuppusamy et al., 2016d). Hence much interest has developed on making remediation solutions even more effective and economical. In this view, US EPA (2001) advises combining different treatment technologies into a unified cleanup strategy. In 2007, US EPA approved a new technology developed by VeruTEK Technologies, Inc. - surfactant enhanced in-situ chemical oxidation that uses biodegradable, food-grade plant extracts such as coconut, castor and soybean oils along with oxidants (persulfate activated with Fe(II)EDTA) to destroy PAHs in soil (US EPA, 2000).

US EPA (2000) estimates that on average an 10,000 m^2 MGP site will cost US$7 million minimum to remediate by excavation and landfilling. The same site estimates US$3-9 million when subjected to in-situ bioremediation, although this is a conservative estimate. Cost estimates for the other technologies are summarized in Fig. 4a. Roughly, contaminated sites range from less than 1,000 to over 100,000 m^2 in size and could cost an average of US$30 million to remediate (Ruttenberg et al., 1996; Ashraf et al., 2014) (see Fig. 4b for the breakdown cost by function). Cost varies from a minimum of US$150,000 to $650,000 for small sites and US$1.5 to $30 million for large sites. Assuming all 58,900 sites are the average global PAH contaminated MGP sites, their minimum cleanup costs in the future would range from US$8 billion to $1 trillion. However, it should be noted that a few sites have already been cleaned up and many smaller ones may require minimal remedial cost. Anyone who can determine cost-effective, environmentally protective means to reduce these costs will have an enormous business opportunity in the MGP site cleanup industry.

More specifically labor costs for approximately 36-61% of the total remedial expense depending on the type of technology adopted and location. Nearly 76-4,750 workers are involved in the remediation of a single site (Eco Canada, 2007). Of these 57% are non-environmental employees or professionals (equipment operators, general laborers, truck drivers and site managers), wherein the remaining 43% is comprised of environmental personnel who are senior, intermediate, junior, analytical chemist, office staff, contractor site environmental health and safety officers. A rough estimate of the number of non-environmental and environmental officers involved in site assessment and remediation of a large contaminated site is summarized in Table 4. It is expected that environmental employment will triple over the next 10-15 years to support direct cleanup of PAH contaminated sites worldwide.

5. Remediation technologies: overview of 1990-2014 research

Various technologies reported in the literature for the remediation of PAH contaminated field soils on bench- pilot- and field-scale during the past 24 years are consolidated and shown in Table 5. They include a range of more widely applied technologies such as heating, soil washing/solvent extraction, chemical oxidation, bioremediation and integrated remedial approaches to new and emerging ones. These include, for example, electrokinetic remediation, enzyme biocatalyst treatment and vermiremediation.

5.1. Established technologies

5.1.1 Incineration and in-situ thermal desorption (ISTD)

Widely applied technologies of PAH contaminated soils have been well reviewed by other researchers (Wilson and Jones, 1993; Mohan et al., 2006; Gan et al., 2009). ISTD also known as conductive heating is effective for separating (volatilizing or destroying) PAHs

from contaminated soils (Gan et al., 2009), coal tar, refinery and wood treatment wastes. Incineration effectively destroys PAHs in the contaminated plume using high temperatures (Chen et al., 2013) ranging between 900 to 1200°C. In 1986, US EPA conducted a remedial investigation of a heavily creosote contaminated superfund site located in Louisiana (Acharya and Ives, 1994). The site remedy included excavation and incineration of 142,000 Mg contaminated solids (soil + sediment + waste piles) in a transportable incinerator. The incineration system destroyed 90% of the total PAHs in 40 months and proved to be successful. Yet the instalment of incinerator off-gas control devices incurred more energy besides cost and was considered to be the major drawback when applying incineration technology (Islam et al., 2012). Like incineration, ISTD uses heat to physically separate PAHs from the soil, however no excavation is required and is considered to be relatively safe and emits little or no PAH compounds into the atmosphere (Kuppusamy et al., 2016d). This is because it involves the use of a carrier gas or vacuum system that sweeps the volatilized PAH compounds into the gas treatment system for secondary or off-site disposal. Using a laboratory unit (thermally enhanced soil vapor extraction reactor with dimension of 48 cm^2 and 30 cm depth) and field pilot studies, Hosseini (2006) demonstrated the feasibility of an in-situ soil venting thermal desorption (SVTD) process for remediating soils containing PAHs associated with lampblack residuals (a byproduct of the utility gas manufacturing process that is commonly found at MGP sites).

In a bench-scale reactor that operated for 35 days, SVTD was successful in mobilizing and subsequently reduced the concentration of most PAHs in a moderate temperature range (250-300°C). Though the proposed technology was successful at bench-scale and combined salient features of ex-situ thermal desorption (volatilizing PAHs from impacted soil zone) with in-situ soil vapor extraction technique (collecting even substantially lowering volatile

PAH compounds generated as hot vapors), extending the SVTD process to pilot/field-scale was challenging owing to the complications posed by soil moisture and heterogeneity.

5.1.2. Solvent extraction/soil washing

Solvent extraction/soil washing (SE/SW) is a viable cleanup technique to treat soils contaminated with HMW PAHs that are not as efficiently removed as expected due to their high hydrophobicity, low bioavailability and slow desorption (Gong et al., 2010). SE/SW is based on the desorption of PAHs from the binding site in (or on) the solid matrix through the action of simple water, organic solvents, surfactants which may be non-ionic/anionic, complexing agent like cyclodextrin (CD), non-toxic and biodegradable flushing agents like vegetable oils or humic acids, followed by elution from the solid into the extraction fluid (Gan et al., 2009; Mousset et al., 2013). The liquid phase containing the desorbed PAHs is then disposed or subjected to further chemical or biochemical treatments for complete detoxification. Conte et al. (2005) proposed natural surfactant - humic acid (HA) as a better choice for soil washing of high PAH contaminated soils than water and synthetic surfactants like sodium dodecylsulphate (SDS) and triton X100 (TX100). Evidently HA exhibited an additional capacity that promoted microbial activity for further natural attenuation in washed soils. Recently, FAME – ‘fatty acid methyl esters’, a major constituent of biodiesel - exhibited better efficiency in removing PAH than their parent compounds (methanol and soybean oil) and other well-known washing agents (CD, HPCD and TX100) (Gong et al., 2010). The percentages of PAH removed from MGP soil with total PAH concentration of 997 mg kg^{-1} were 59%, 46% and 51% for the FAME:MGP soil ratios of 1:2, 1:1 and 2:1, respectively. The authors suggested growing plants that can produce FAME for remediation of high PAH contaminated land. Further, vegetable oils can offer many applications in PAHs remediation ranging from its utilization as an environmental-friendly solvent to physically

extract PAHs, and using it as a soil amendment to enhance biological treatments. Vegetable oils are a strong sorption medium of hydrophobic PAHs and their free fatty acids with molar solubility ratios for PAHs are similar to those of synthetic surfactants (Gan et al., 2009). To date, Yap et al. (2010) conducted a brief review on the application of vegetable oils (peanut, sunflower, rapeseed, soybean, palm kernel, corn and canola oil) in the treatment of PAH-contaminated soils. Related studies are listed in Table 5.

5.1.3. Chemical oxidation (ISCO)

One of the in-situ treatment technologies able to degrade both LMW and HMW PAHs in field soils is ISCO. ISCO aims to degrade PAHs after their reaction with an oxidant injected into the soil (Lemaire et al., 2013). Different types of oxidants have been investigated ranging from the more commonly used ozone and Fenton's reagent to less common ones such as potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), sodium (Na^{2+}) or iron (Fe^{2+}) activated persulfate and peroxy-acid (Cheng et al., 2016; Kuppusamy et al., 2016d). The use of Fenton's reagent to possibly desorb or degrade PAHs from soils was reviewed in detail by Yap et al. (2011). At pilot-scale, Liu et al. (1993) and Pradhan et al. (1997) achieved 70-95% PAHs mineralization of MGP soils in slurry reactors treated with 2.5% H_2O_2 and Fe^{2+} solution.

A comparison of oxidants including persulfate, magnetite-activated persulfate, soluble Fe^{2+} activated persulfate to treat former coking plant site soils contaminated with higher concentration of 16 PAHs (1300-1400 mg kg^{-1}) with and without extraction pre-treatment was carried out by Usman et al. (2012). The authors found that the best removal percentages (50-60%) were achieved only in the pretreated field soils with the use of magnetite-activated persulfate without the formation of any toxic by-products because magnetite was a most effective and stable catalyst compared to Fe^{2+} aiding heterogeneous catalytic oxidation of

PAHs. Extraction pre-treatment increased the bioavailable PAH fractions. No PAH abatement was observed in real soils which were not subjected to pre-treatment. Their analysis indicated that availability of PAHs was the most critical factor for degradation efficiency irrespective of the type of oxidants used. In a similar study, Lemaire et al. (2013) also concluded that low availability of PAHs, partly sequestered in the aged soil is the most limiting factor in degradation processes. Recently, Ranc et al. (2016) reviewed the importance of the selection of oxidant doses for successful chemical oxidation of soils contaminated by PAHs.

5.1.4. Bioremediation

One treatment technology that has gained wide approval for the treatment of PAH contaminated soils is bioremediation. Indeed bioremediation is considered to be safe, eco-friendly and economical without simply enacting the transfer to another medium (Mohan et al., 2006; Kuppusamy et al., 2016d). The biodegradation aspects of PAHs have been well reviewed (Juhasz and Naidu, 2000; Haritash and Kaushik, 2009; Duan et al., 2013). Bioremediation of PAH contaminated field soils includes both in-situ (land farming, biostimulation, bioaugmentation, composting and phytoremediation) and ex-situ (bioreactors) treatment options (Kuppusamy et al., 2016d; Kuppusamy et al., 2016e). On-site, the activity of the degrading organisms is largely influenced by fluctuating weather conditions (Kuppusamy et al., 2016a). Meanwhile, the use of bioreactors off-site offers better control of temperature and pressure to enhance the degradation process of PAHs in soil (Gan et al., 2009).

Land farming involves the use of traditional agricultural practices such as tilling, bulking (provides aeration and promotes soil homogeneity for biodegradation), irrigation (provides moisture) and fertilizer application (provides nutrients to enhance the population of

PAH degraders). It has a distinctive advantage for stimulating the indigenous microbes (Wang et al., 2016), however, it is constrained in its degradation efficiency by limiting factors such as the fewer PAH degraders, superficial treatment (soil layer of 10-35 cm), poor contaminant uptake and low bioavailability (Mohan et al., 2006). Hansen et al. (2004) conducted a pilot-scale study at a wood-treatment site contaminated with approximately 13,000 mg kg^{-1} PAHs. They determined that traditional landfarming practice is a useful low-cost treatment technology for restoration of PAH contaminated sites provided there are no time-pressures.

In the case of treatment sites that lack nutrients, ***biostimulation*** (addition of nutrients) has been implemented as a best option to speed up the treatment process (Mohan et al., 2006; Kuppusamy et al., 2016d; de Souza Pohren et al., 2016). Taylor and Jones (2001) demonstrated that nutrient addition alone to soils containing coal tar in both laboratory and field-scale failed to significantly enhance biodegradation of coal tar PAH. However, after 55 days the addition of biodiesel (readily biodegradable with low phytotoxicity) with inorganic nutrients resulted in enhanced degradation of a number of PAH components over the nutrient-only treated samples. The increase in PAH biodegradability by the biodiesel treatments was ascribed to tar solubilization and dispersion, thereby increasing PAH bioavailability and its subsequent uptake by indigenous biodegraders.

Bioaugmentation (i.e. the addition of contaminant degraders cultured at laboratory) is the best option when the soils to be bioremediated constitute very low populations of indigenous PAH degraders (Catiglione et al., 2016). It can be either facilitated by aerobic or anaerobic organisms; however, aerobic bioremediation is widely documented as the majority of laboratory cultured PAH degraders are aerobic Gram positive or negative bacteria and fungi (Kuppusamy et al., 2016f,g,h; Mao et al., 2016). Microbial consortia of bacteria, fungi and bacteria-fungi complex isolated from aged oil-contaminated soil was shown to degrade

PAHs to a high level (45-56%) in both soil- and slurry-phase by Li et al. (2008). The authors observed rapid and extensive degradation of 2-3 ring PAHs than 4 and more ring compounds and suggested the need for pretreatments (preferably chemical pre-oxidation) to enhance the bioavailability as well as removal efficiency of HMW PAHs in field soils. The fungal mycelium was found to have a high surface area, which maximized both mechanical and enzymatic contact with insoluble substrates and invaded a large volume of soil, which resulted in high levels of PAHs degradation observed with the fungal consortium over the other two.

The intrinsic depuration potential of a soil contaminated by PAHs originating from a contaminated industrial site was evaluated by Pinelli et al. (1997). They employed a different aerobic batch known as bioreactors: a slurry-phase and two semisolid-phase (blade-agitated and rotary vessel) bioreactors. Of the three the slurry-phase system provided the most effective (40-89%) and fastest (2-14 days) removal of the PAHs and the organic extractable matter. The PAH degradation was attributed to the activity of indigenous aerobic specialized bacteria, higher pollutant desorption rate, homogeneity and oxygen mass transfer in the slurry-phase system with respect to the semisolid-phase ones.

Interest has increased concerning the use of ***composting/biopiling*** as it has shown to be effective in degrading PAHs (Mizwar et al., 2016). Antizar-Ladislao et al. (2004) had reviewed the bioremediation of PAH contaminated wastes using composting approaches. In one field investigation, Guerin (2000) stated that use of fresh organic matter, maintaining constant moisture in the soil-compost mix and ensuring the homogenization of the soil to be composted can effectively compost PAH compounds in soils (Table 5). Under these conditions, Guerin witnessed over 50% of HMW PAH being removed over 210 days. A pilot-scale attempt to treat a challenging high alkaline soil (pH = 12.8) contaminated with 200 mg kg^{-1} PAHs by composting with sewage sludge and yard waste was undertaken by Moretto et

al. (2005). The process was carried using a closed tank with forced aeration for a period of 60 days, followed by 70 days with natural aeration. Under controlled temperature, electrical conductivity, C and N contents, and effective pH neutralization a progressive drop in the PAH concentration was observed. After 130 days the overall PAH degradation percentage was 68%. The use of biopile to remediate an aged soil polluted with 3.6 mg kg^{-1} PAHs under field conditions was described by Maletic et al. (2009). The rate of biodegradation depended on the thickness of the soil layer. In the upper and thinner soil layer of the biopile, oxygen and water transport were facilitated and the rate of biodegradation was higher than in the lower and wider layers. PAH concentration decreased to about 77% in 500 days and the most rapid degradation was obtained for PAHs with fewer rings.

Plant assisted bioremediation (***Phytoremediation***) is one in-situ decontamination approach that can potentially address PAHs contamination at field-scale (Petruzzelli et al., 2016). PAH degradation enhancement by plants was investigated since it was known that plants could: accumulate/sequester/chemically transform contaminants in the soil; secrete enzymes that can act as a surfactant to increase the bioavailability of the pollutant; improve the nutrient status of the soil; and interact synergistically with soil microenvironment, and in fact improve the xenobiotic-degrading abilities of rhizospheric microorganisms (Roy et al. 2005; Gan et al., 2009). Highly adaptable plants with deep and large root surface areas and requiring less maintenance are generally preferred (Alagic et al., 2016).

To promote the PAH dissipation of soil by phytoremediation, Sun et al. (2011) suggested intercropping alfalfa (*Medicago sativa*) and tall fescue, as the use of different plants may result in diverse microbial groups in the rhizosphere that exert different effects on soil PAHs. The 7-month field experiment (initial soil PAH = 546-817 mg kg^{-1}) showed that PAHs in intercropping (31%) were significantly higher than in monoculture (20%) or unplanted soils (0%). Meng et al. (2011) also suggested that certain multispecies mixtures

(ryegrass, white clover – *Trifolium repens* and celery - *Apium graveolens*) facilitate the phytoremediation of PAH contaminated soils over monocultures. Furthermore the major pathway of PAH phytoremediation enhanced plant-promoted biodegradation (Sun and Zhou, 2016), whereas plant uptake had only a minimal effect.

Another way to improve phytoremediation is through the use of plant growth promoting rhizobacteria (PGPR) that generally has the ability to relieve environmental stress in plants and in doing so, increase plant survival under less than ideal conditions (de Boer and Wagelmans, 2016). PGPR stimulates plant root development and enhances root growth. Besides, the mechanism of nitrogen fixation, synthesis of siderophores, production of phytohormones and solubilization of minerals by PGPR enhances soil fertility as well as the overall development of the phytoremediating plant. Huang et al. (2004) confirmed the PGPR (*Pseudomona putida, Azospirillum brasilense* and *Enterobacter cloacae*) accelerated plant growth, especially roots in heavily contaminated soils, diminishing the toxic effects of PAHs on plants. The increased root biomass in PGPR treated wild rye (*Elymus canadensis*) plants led to a more effective remediation of 90%. Teng et al. (2011) observed a synergistic association existing between alfalfa and *Rhizobium* that stimulated the rhizosphere microflora, making it possible to degrade 51% PAHs (initial concentration = 10 mg kg^{-1}) in 90 days.

5.1.5. Integrated approaches

Although the above physical, chemical and biological treatments have been shown to be effective in treating PAHs, there are still limitations in applying them to remediate field soils (Kuppusamy et al., 2016d). These include reduced effectiveness in remediation of aged soils particularly HMW PAHs, accumulation of transformation products, higher process duration and cost. To address these limitations, various combinations of integrated treatments: physical-chemical (for instance, solvent extraction + chemical oxidation),

physical-biological (for instance, solvent extraction + bioremediation), chemical-biological (for instance, chemical oxidation + bioremediation), biological-biological (for instance, enhanced bioremediation – bioaugmentation + biostimulation) and physical-chemical-biological (for instance, soil washing + chemical oxidation + bioremediation) can be used to treat PAHs in soils (see Table 5).

Dadkhah and Akgerman (2002) reported on combined extraction/in-situ oxidation using subcritical hot water. The process, however, operated in series. The contaminated field soil was packed in a reactor and PAHs were semi-continuously extracted with subcritical hot water. Simultaneous pumping of H_2O_2 into the hot water reaction vessel resulted in negligible concentrations of PAHs in the soil via oxidation. The authors suggested that this integrated method is relatively cost-effective as no organic solvents are needed during treatment and water was cheap, easily available, inflammable and non-toxic.

Bogan et al. (2003) studied the influence of adding corn and palm kernel oil to overcome limited mass transfer and thereby enhance the efficiency of PAH degradation using Fenton treatment. Adding vegetable oil (5% on dry weight basis) significantly enhanced PAH removal (15-45%) from highly contaminated aged soils. The outcome was more significant for HMW PAHs. However, the overall remedial efficacy of the integrated approach was low (20-49%) for 2-3 h soil/oil contact time and 5-14 days of Fenton treatment. The study showed that to enhance Fenton treatment, the addition of oil should be adequate to facilitate the mass transfer of PAHs into lipid aggregates. In an early study, Lee et al. (2001) presented the use of 100 mL of 100% ethanol or acetone for 1-2 days to enhance the PAHs' bioavailability in coal tar contaminated soil prior to aerobic biodegradation in a bioreactor. Solvent pretreatment of soils enhanced the rate of biodegradation resulting in 90% total PAHs degradation in 17 days. However, those that did not receive pretreatment took nearly 35 days to achieve similar degradation efficiency.

The reaction rate with solvents was directly proportional to the aqueous solubility of 4- and 5-ring PAHs particularly chrysene and benzo[a]pyrene. The residual solvent that remained after evaporation in the soil may have acted as a growth substrate leading to an increase in the population of indigenous PAH degraders, thus documenting the preferential removal of HMW PAHs. Observed enhancement in the availability of PAHs was driven by the distribution of PAHs between the solvent and the soil and was independent of soil physical properties. The Institute of Gas Technology in the United States developed and demonstrated an integrated bench- and field-scale chemical-biological treatment (CBT) process employing aerobic biodegradation with Fenton oxidation to efficiently remediate soils and sludge contaminated with PAHs (Srivastava et al., 1994).

It was found that this CBT process efficiently removed 16 PAHs at both batch and field-scales with removal efficiencies of 98 and 50%, respectively. In the field experiment, comparatively less degradation per cent over the bench-scale study was observed due to the decrease in total and PAH-degrading microorganisms by the drop in soil pH after chemical treatment. Neutralization of pH (lime additions) was suggested to be helpful in overcoming such limitation. Further environmental conditions that kept fluctuating (temperature and rainfall) were also considered as one of the major limitation that decreased the biodegradation activities of the microbial community. In another study, Nam et al. (2001) examined biodegradation by microbial consortium followed by Fenton treatment in MGP soils. The coupled technique was superior over individual treatments. Recalcitrant 4-5 ring PAHs were reported to be removed by Fenton oxidation and biodegradation that targeted 2-3 ring PAHs removal. Thus when LMW PAHs-dominated biodegradation was recommended as a pre-treatment strategy, in the case of dominant HMW PAHs, chemical oxidation is a feasible pre-treatment option (Yap et al., 2011).

Using biodegradation as a final step after chemical oxidation with initial physical treatment has been demonstrated. For example, Haapea and Tuhkanen (2006) pre-treated field soil with washing (using water) and ozonation before bioaugmentation (addition of a *Pseudomonas* strain) and biostimulation (addition of artificial nutrients – source of NPK). Three different oxidant doses with subsequent soil washing were tested at different pH levels to assess their influence on PAH (bio)degradation. In the experiments carried out, consumption of oxidant was 5-10 times less in the integrated treatments than individuals. Also the removal of 90% of PAH was only achieved in the coupled treatments compared to the methods that were tested as single. One of the limitations in the application of this integrated technology full-scale is the increase in treatment cost due to the necessity to adjust pH, which declines drastically following pre-treatments and subsequently restrict PAHs biodegradability. The impact of pre-treatments on the degradation products and intermediates that are sequestered in the soil matrix was not investigated, which could serve as a possible subject of future research before the technology develops further.

5.2. Emerging technologies

Recently, electrokinetic remediation, enzyme-mediated bioremediation, multi-process phytoremediation and vermiremediation have been employed in the treatment of PAHs contaminated soils (Kuppusamy et al., 2016d,e). Notably, existing research on the application of vermiremediation (Ekperusi and Aigbodion, 2015) to treat PAHs contaminated soils is very limited. There are wider avenues to investigate the use of these new remedial approaches in conjunction with the established physical, chemical and/or biological treatments to achieve maximum PAH removal efficiency.

5.2.1. Electrokinetic remediation

Electrokinetic remediation is useful for the treatment of low hydraulic permeability soils, where other techniques such as natural attenuation are not adequate (Pazos et al., 2010). This technique involves the application of a low intensity direct current through the soil between appropriately distributed electrodes. Ionic pollutants are transported to the oppositely charged electrode by electromigration. Moreover, electroosmotic flow provides a driving force for the movement of soluble pollutants (Reddy et al., 2006). Though electrokinetic remediation is a well-established technique, its use in PAH remediation is not proven at pilot- or field-scale. The hydrophobicity and slow desorption rates of PAHs make it difficult to remove them from subsurface environments using the traditional electrokinetic approach. Hence, recently solubilizing agents such as surfactants, co-solvent and cyclodextrins are considered to enhance the efficiency of removing PAHs from field soils using in-situ electrokinetic technique.

During the electroremediation process, these agents can be added directly into the soil or to the electrode chamber solutions and then they are introduced into the soil by electro-osmosis and/or electromigration (Pazos et al., 2010). Reddy et al. (2006) carried out a series of bench-scale electrokinetic experiments using different flushing agents (surfactants – 3% Tween 80 and 5% Igepal CA-720; co-solvent – 20% n-butylamine; cyclodextrin – 10% HPCD) to extract 16 PAHs from aged MGP soil. The experiments were conducted at 2 VDC cm^{-1} voltage gradient and 1.4 hydraulic gradient. They found that after 20 days of treatment the most effective flushing agent, surfactant (Igepal CA-720), proved to be the most efficient in removal due to partial solubilization of PAHs, causing some PAHs to migrate towards the cathode. Based on the contaminant mass that remained in the soil, further optimization of the electrokinetic system - depending on the soil matrix - was necessary to improve the PAH removal efficiency for the field soils.

Indeed, it should be possible to combine electrokinetic movement of PAHs with their biodegradation in-situ, thereby overcoming some of the biological constraints to degradation associated with soil heterogeneity and hotspots of contamination. Isosaari et al. (2007) developed an electrokinetic test cell assisted by an oxidizing agent, persulfate, to treat creosote-contaminated clay (total 16 PAHs concentration = 420 mg kg^{-1}). After 8 weeks, it was observed that 35% PAH was removed in the presence of electroremediation with persulfate oxidation compared to a poorer degradation efficiency of 12-20% in the presence of either electrokinetics or persulfate oxidation alone. A combination of electrokinetics with Fenton oxidation was not better than electrokinetic treatment alone. Furthermore it was shown that the efficiency of PAHs removal when utilizing this integrated approach is dependent on the reagent dose applied voltage gradient and ratio of direct and alternate voltages.

5.2.2. Enzyme-mediated bioremediation

The catalytic actions of microbial enzymes is a ‘green’ approach that is extremely efficient and selective compared to chemical catalysts due to fewer reaction conditions, higher reaction rates, greater stereo-specificity and the ability to catalyze reactions at relatively low temperature and wide pH range (Mohan et al., 2006). Application of enzyme biocatalyst treatment in the remediation of PAH contaminated soil has recently found its place. Laccase from a fungus, *Trametes* sp., was studied to evaluate its potential to oxidize 15 priority PAHs-contaminated field soils in a sole substrate system in the presence of 2,2’-Azino-bis-3-ethylbenzthiazoline sulfonate as mediator (Wu et al., 2008). Results documented the enzymatic transformation of PAHs into comparatively less toxic intermediate (for instance, anthracene to anthraquinone and BaP to benzo[a]pyrenyl acetate), indicating the applicability of fungal oxidation (Table 5). When the enzyme was amended more (10 U g^{-1})

the PAH degradation was higher. On day 1, with 10 U g^{-1} laccase nearly 24% PAHs were degraded. Notably by the 14th day more than 80% BaP disappeared. However, one of the limitations in the wider application of enzymatic bioremediation is its financial constraints. Immobilization, improvement of extraction and purification followed by optimization of physico-chemical factors may reduce the expense associated with enzyme techniques.

5.2.3. Multi-process phytoremediation

As biological treatment is eco-friendly and cost-effective, some of the researchers aim to couple two or more bioremediation technologies in order to enhance PAHs degradability and reduce treatment time. To improve phytoremediation processes, several techniques that comprise different aspects of PAH removal from soils have been combined by Huang et al. (2004). The authors developed a multi-process phytoremediation system composed of physical (volatilization), photochemical (photooxidation), microbial and phytoremediation processes. The techniques applied to implement the above processes were landfarming (aeration and light exposure), introduction of contaminant degrading bacteria, PGPR and plant growth of contaminant tolerant tall fescue. Over 120 days this multiprocess remediation system removed 40-50% more PAHs compared to individual techniques.

5.2.4. Vermiremediation

Most soils contain a majority of pores with diameters of ≤ 20 nm. Such pores are too small to allow the bacterium (1 µm), protozoa (10 µm) or root hairs (7 µm) to penetrate and attack the chemicals. PAHs existing in such fine soil pores are not ‘bio-available’. In such cases, earthworms play a significant and acute role by enlarging the pores through continuous ‘burrowing actions’ in the soil, thus allow the microbes to enter into the pores and act on PAHs (Ma, 1995). In addition, earthworms either dermally (passive diffusion through outer

membrane) or intestinally (passes through the gut by digestion) absorb PAHs from soil and biotransform or biodegrade the ingested hydrocarbon, rendering them harmless. Meanwhile the quality of the soil is improved significantly in terms of physical, chemical and biological properties as the worms thoroughly upturn and disperse the soil, ingest large volumes of soil and excrete nutritive materials in the form of 'vermicasts' along with proliferation in the population of beneficial soil microbes including nitrogen fixers (Sinha et al., 2002; Chaoui et al., 2003).

With the passage of time, remedial actions can be intensified as worms reproduce rapidly and could possibly achieve enhanced degradation of PAHs. In general, vermiremediation - being self-driven, requiring little or no energy, easy to construct, operated and maintained technology, may prove to be an economical and environmentally sustainable in-situ approach to remediate sites contaminated with PAHs in less than a year (Sinha et al., 2008). Bioaccumulation of PAHs in earthworms (*Eisenia foetida* and *Lumbricus terrestris*) from contaminated soils obtained from a disused manufacturing gas plant was studied by Parish et al. (2006). Their results showed that earthworms can readily accumulate 0.08-0.2 mg kg^{-1} of 3-4 ringed PAH compounds. However neither species accumulated measurable quantities of 5-6 ring PAHs.

In a case study, Sinha et al. (1998) confirmed that earthworms (mixture of *E. fetida, E. euginae* and *Perionyx excavates*, varied in age and size) enhance PAH removal from highly contaminated gas work site soil (total PAH concentration = 11820 mg kg^{-1}) by any of the following mechanisms: bioaccumulation, enzymatic degradation or microbial degradation. Nearly 70-90% of seven HMW PAHs were removed in 12 weeks with a loading rate of about 50 worms per kg soil in a treatment that received kitchen waste (5 kg contaminated soil + 2 kg bedding material with worms + 5 kg kitchen waste). It proved to be more efficient than treatment that received worms + cow dung (PAH removal = 70-85%) and compost alone

(PAH removal = 30-60%). The authors suggested that an increase in loading rate to 100 worms per kg soil might have resulted in 100% removal of the PAHs. Several studies indicate that earthworms are sensitive to high contaminant and/or co-contaminant levels and fluctuating environmental conditions (Sverdrup et al., 2002; Spurgeon et al., 2005; Jonker et al., 2007).

Hence, vermiremediation may not be suited for field treatments and is restricted to remediation of low to medium contaminated soils in microcosms. In future, scholars can investigate the suitability of vermicomposting as an example of a green and sustainable approach for treating PAH contaminated soils at field-scale.

5.3. Current trend

It is evident that of all the available remedial options, bioremediation followed by its integration with other approaches has gained wider approval as feasible technologies for the treatment of age-old PAHs-contaminated soils in the following order: bioremediation > integrated technologies (physical/chemical/biological) > chemical oxidation > solvent extraction > heating > electrokinetic remediation (see Fig. 5a). Among the bioremedial approaches that are available, a majority (~33%) of the PAH-contaminated field soils had been remediated by solid-phase treatment followed by the use of phytoremediation (22%), bioreactors (22%) and composting (13%) as shown in Fig. 5b. Furthermore the second most commonly implemented integrated technologies were used in the following order: biological-biological > chemical-biological > physical-chemical > physical-chemical- biological ≥ thermal-chemical treatments (Fig. 5c). Although biological approaches are popular, soils contaminated with high PAH concentrations, for instance > 10,000 mg kg^{-1} (hot-spots) will not be amenable for most bioremediation approaches if pretreatment is not first employed to reduce PAH concentration and toxicity (Khodadoust et al., 2000). In the case of such high

PAH contaminated soils either incineration, thermal desorption, solvent washing or chemical oxidation is only feasible or is necessarily executed as pre-treatment options.

6. Constraints

The current trend clearly depicts the interest of researchers in green and sustainable approaches. Although most green or bioremediation technologies discussed in this review have been recognized for more than a century as being able to successfully remediate PAH-contaminated soils, in most cases the remediation strategies fail at field-scale due to several factor-based limitations (Fig. 6). These can be broadly grouped into technical and non-technical factors.

6.1. Technical factors

Technical factors affecting remediation can be broadly grouped into four interrelated classes: soil and weather-related, microbial-related, contaminant and co-contaminant-related and cost-related. PAH location in the soil profile and the spatial distribution of PAHs throughout a site are important points to consider. The constraints are site-specific. Briefly dynamic interaction of factors, viz., type of environment (soil), aeration status (oxygen availability), PAH concentration, temperature, bioavailability of subsidiary carbon source, presence of other inhibitory pollutants or co-contaminants, soil water content, water activity, lack of soil nutrients and microbial competition greatly influence the efficiency and effectiveness of a remedial system (Christofi and Ivshina, 2002). Proper optimization of factors is essential to enhance the remedial efficiency and ensure success at field-scale (Tang et al., 2005). One of the most limiting factors that determines the remedial efficiency is contaminant bioavailability. Generally HMW PAHs possess low aqueous solubility, high solid-water distribution ratios and are more stable due to their angular ring arrangement,

which count against its bioavailability in the soil matrix, mass transfer and subsequent metabolism by microorganisms (Mohan et al., 2006). The higher the HMW to LMW PAH ratio, the greater is the toxicity, there is also less bioavailability and as a consequence the rate of degradation is slower.

Yet the available techniques are not successful in the complete degradation of HMW PAHs under diverse soil conditions. Bioavailability that is influenced by physico-chemical properties of both PAHs (chemical structure, molecular weight, concentration and toxicity) and soil (composition, texture, moisture pH, sorption, occlusion and ageing) strongly affects the feasibility of risk-based remediation, type of microbial transformation occurring and whether PAHs will serve as a primary, secondary or co-metabolic substrate or energy source (Boopathy, 2000). The bioavailability issues can be overcome through the use of surfactants, which increase the PAH bioavailability for microbial degradation (Adrion et al., 2016). Research has indicated that biosurfactant producing organisms (bacteria and fungi) and their surface active compounds can be used to speed up the remediation of mixed contaminated soils. However, little work has been done on its use for the field remediation of PAH contaminated soils and this is probably related to the high production costs for biosurfactants. A more basic understanding of PAH solubilization by the use of these compounds, physical, chemical and biological interaction of biosurfactants with other factors and its cost-effective production is required for its wider application in the field (Christofi and Ivshina, 2002; Bezza and Chirwa, 2016).

Another current limitation is the inability to measure and control the biochemical pathways in complex soil environments. To achieve desirable results at large scale, it is mandatory to evaluate the biochemical conversions (which may be favorable or unfavorable) in terms of whether individual or mixtures of PAH compounds are removed, whether toxicity is a result of the remediation process and whether the element in the parent compound are

converted to measurable non-toxic metabolites (Boopathy, 2000). Such biochemical activity can be controlled only under optimized conditions which in most cases are not focused. Further, selecting the right remedial system also determines the rate and extent of the cleanup process. For instance, although in the case of solid-phase treatments the degradation process is too slow, bioreactors are known to support effective PAH degradation in soil matrix by counteracting the consequence of mass transfer and thus facilitating an increase in bioavailability by using optimized conditions (Mohan et al., 2006). Thus, depending on the severity of contamination and remedial objectives, choice of in-situ or ex-situ remediation has to be carefully considered along with the type of pre- and/or post-treatment options. Additionally new approaches can be developed integrating the significant features of individual techniques which has more scopes for exploration. However, cost of remediation which is the most limiting factor has to be well thought-out in such cases.

Inappropriate remediation objectives (including time, socioeconomic aspects and human health), lack of managed maintenance and monitoring are also causes of failure. Successful bioremediation chiefly depends on the choice of right microbes (Boopathy, 2000; Kuppusamy et al., 2016f,h). So far in most cases bioremediation of PAH contaminated soils has failed because for the following reasons: more indigenous PAH degraders, efficiency of indigenous or introduced strains (bacteria, fungi or algae) to degrade HMW PAHs, toleration of co-contaminants like heavy metals, self-assimilating essential nutrients (PGPR activity – N-fixers, P solubilizers), ability to withstand fluctuating weather conditions (for instance, tolerate low to high temperature, salinity and pH) or producing compounds such as enzymes, surfactants and emulsifiers that can enhance desorption and hence increase the bioavailability of PAHs in sequestered soils (Kuppusamy et al., 2016g). In some cases, indigenous microbes suppress the introduced strains which may also result in the failure of large-scale remediation of PAH contaminated soils inspite of augmentation using laboratory defined successful

microbial inoculum. Hence in order to overcome the microbe-related limitations it is necessary to standardize the growth parameters of PAH degraders carefully at bench-scale.

6.2. Non-technical factors

In addition to technical constraints, some of the non-technical factors such as favorable public and regulatory perception, ability to meet time limitations and acceptable risks in residual contaminants remaining after remediation also affect the cleanup process. Regulations not only drive the cleanup of contaminated soils, but also limit the use of some remedial approaches. One notable example is the use of genetically modified organisms (GMOs) which is currently being debated for their acceptance (Pisciotta and Dolceamore, 2016). Environmental laws and regulations also control the remediation process (how equipment can be used to accomplish specific management objectives) and its market value. Though more intensive research is required for the cleanup of PAH contaminated soils, funding or grants for conducting basic research is slowly declining. Yet official criteria for evaluating the success or failure of a particular strategy at site conditions have not been established. A successful remediation program requires a multidisciplinary approach which in most cases is not offered, i.e. integrating microbiologists, geologists, engineers, hydrogeologist and soil scientists along with the stakeholders. Universities and/or private institutes can offer more training to help individuals acquire combined expertise in the remedial field. Unlike other sectors, remediation does not result in the production of value-added products. Hence venture capital has been slow to invest and as a consequence commercial activity in R&D has lagged far behind other industrial sectors. Also greater risk from the liability standpoint is believed to prevail according to Boopathy (2000).

In general, site remediation is a (non)technically intense process which has to be carefully planned and executed. Every remedial option has to be forcibly tailored to site-

specific conditions using treatability studies on a small scale before the actual cleanup of the sites can commence. Both site characterization and treatability studies have to answer some of the following questions before field-scale implementation in order to overcome the failures:

- ► does degradation occur naturally? Are the contaminants biodegradable and does microbial metabolism produce toxic metabolites?
- ► are environmental conditions appropriate for degradation?
- ► do risks exist after remediation?
- ► is there a necessity for pre- and post-treatment? If so what are the suitable technologies? Are there enough funds to implement such treatments?
- ► if the pollutant does not degrade completely, where it will go?

7. Directions for future research

Some recently advances in innovative remedial approaches that are mostly biological and expected to give rise to an 'era of green biotechnology' in the near future are nanoremediation, transgenic approaches and photo-hetero microbial systems. These emerging technologies have successfully remediated a number of organic and inorganic pollutants (Kuppusamy et al., 2016d; Kuppusamy et al., 2016e). However, their potential to remediate PAH contaminated soils are still unexplored and hence could be the focus of future research in order to develop a rapid, reliable, low cost and risk-based PAH cleanup strategy.

7.1. Mixed cell culture system

Consortia of bacteria, bacteria and fungi or bacteria and algae are currently being developed and utilized for environmental remediation (Kuppusamy et al., 2016a; Sharma et al., 2016). To overcome the microbe-related limitations at real contaminated sites in the

presence of mixed high contaminant levels, ‘engineering microbial consortia’ (Brenner et al., 2008) could be developed and used in the near future. Use of algal–bacterial consortia is much more beneficial than bacterial consortia, or bacterial–fungal consortia in the remediation of pollutants (Subashchandrabose et al., 2011). This is because cyanobacteria or microalgae release a variety of light weight compounds and extrapolymeric compounds composed of nucleic acids, lipids, proteins, excretion products and fermentation products that serve as microbial growth substrates which, in turn, enhance the degradation potential of aliphatic and aromatic contaminants by the bacteria (Kirkwood et al., 2006). Also, microalgae supply oxygen for enhancing aerobic degradation of contaminants (de Llasera et al., 2016). Hence future research can focus on the development and testing of the algal-bacterial consortia of strains that are able to degrade HMW PAH, tolerate co-contaminants as well as adverse weather conditions and produce biosurfactants. Developing an inoculum of such superbugs will ensure bioremedial success at problematic MGP sites.

7.2. Green nanoremediation

Of late, nanoremediation has become a major subject of research and development with great potential for contaminated site cleanup and protecting the environment from pollution (Kuppusamy et al., 2015). The small size (1 to 100 nm size) and novel surface coatings of the nanoparticles enable them to be more widely distributed in comparison to larger-sized particles, and this unique property makes them best suited for in-situ applications (Tratnyek and Johnson, 2006). It enables remediation in deeper soils and is compatible even with other technologies like bioremediation and aid as an expanding tool for contaminant cleanup (Huang et al., 2016). The development and use of nanofertilizer (biostimulation + bioaugmentation), nanominerals (biostimulation) or green synthesized nanooxidizers (PAH oxidation) could be explored to properly exploit the massive significance of nanoremediation

in PAH removal. Besides this, nanoremediation can be integrated with some established PAH bioremedial approaches to enhance the remedial efficiency and attain rapid PAH degradation under field conditions.

7.3 Transgenic approaches

Advances in protein and genetic engineering techniques have opened up new avenues for the development of genetically modified microorganisms (GMOs) and plants to function as ‘exclusive biocatalysts’ in which certain desirable enzymes or degradation pathways from diverse organism are brought together in a single host with the aim to perform specific reactions (Van Aken, 2009; Demain and Vaishnav, 2009). In genetic engineering, catabolic genes associated with insertion sequences are rapidly disseminated or DNA is shuffled among the microbial groups to expand the novel degradative pathway (Maestri and Marmiroli, 2011). Engineering of catabolic enzymes enhances the degradative rates or broadens the substrate specificity. When a single strain is constructed by genetic engineering to perform a number of related or unrelated metabolic activities, the predictability and efficiency of the process gets significantly enhanced and the recombinant organism is able to degrade a wide range of recalcitrant pollutants rapidly within a shorter time period. Even the use of genes that encode the biosynthetic pathway of biosurfactant could improve the rate of biological degradation by increasing the pollutant bioavailability in the natural ecosystem. Also, the genes conferring resistance to critical stress factors enhance both the survival and performance of the designed catalyst (Dua et al., 2002).

However, there is a problem with the introduction of GMOs into the environment due to legal restrictions on their release into the natural ecosystem, additional energy needs imposed by the existence of engineered genetic materials in the bacterial cells, and the low survival of the foreign strains that have been introduced into the real problematic lands (Maiti

and Maiti, 2011). Such judicial blocks can be overcome by utilizing plants rather than microorganisms as 'engineered environmental biosystems'. In this view, the emerging multiprocess phytoremediation system could be further facilitated by GM plants containing transgenes that are responsible for metabolism of PAHs and simultaneous removal or immobilization of inorganic co-contaminants such as heavy metals in mixed contaminated soils that are found in MGP sites. Along with the introduction or overexpression of PAH degrading or co-contaminant resistance genes in GM plants, use of crop breeding and seed coating technology (promote germination of hyperaccumulating plants) can be integrated to achieve rapid remediation.

Currently there is no convincing GMO for such a purpose. Also there has not been much public acceptance of GM plants, and their ecotoxicological or ecological consequences are far from being satisfactorily addressed. A key point is that the potential impacts of the developed GM plants should be addressed by demonstrations with long-term experiments that may gradually increase public acceptance. Further, coupled green approaches such as mixed cell culture system with biosurfactant flushing or rhizoremediation, vermicomposting with bioaugmentation and nanoremediation with phytotechnologies, etc. can be aimed to counteract the current challenges and upgrade the existing and emerging technologies.

8. Conclusions

A large number of technologies are still at the prototype level while others have been applied in practice to cleanup PAH polluted sites. However, they are not capable of solving the PAHs issue. Successful commercial options are heating, extraction, oxidation and selected bioremediation systems. This is because each PAH contaminated site case is different, and the way to manage it requires careful weighing of all relevant factors (Fig. 6), along with the limits set by the remediation policy, available financial support and public

acceptance. As green remediation is of interest and bioremediation is what people prefer, what is now important is to investigate the future directions proposed in this review as well as gain a better understanding how microbial communities co-operate. The studies on the structure and functions of microbial communities in the polluted sites on different spatial and temporal scales and their responses to different stimuli using community fingerprinting and environmental genomics techniques can show the way (Megharaj et al., 2011). It is impractical to restore all natural functions of PAH polluted soils and not every site can ever be completely recovered to a pristine state given the cleanup of background conditions. Hence, the application of the principle of function-directed risk-based green remediation approach may be enough to manage long-term PAH contaminated soils.

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Fig. 1. PAHs – Global emission sources and concentration in soil over time

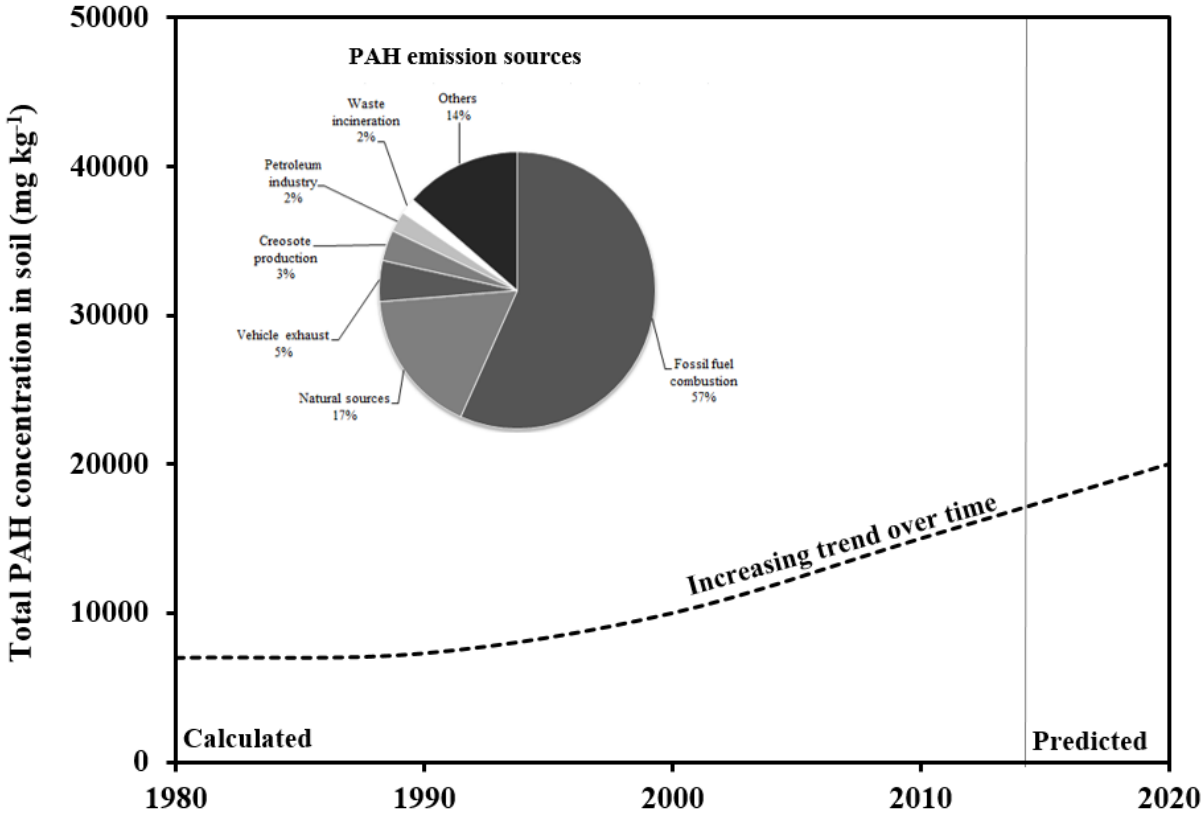
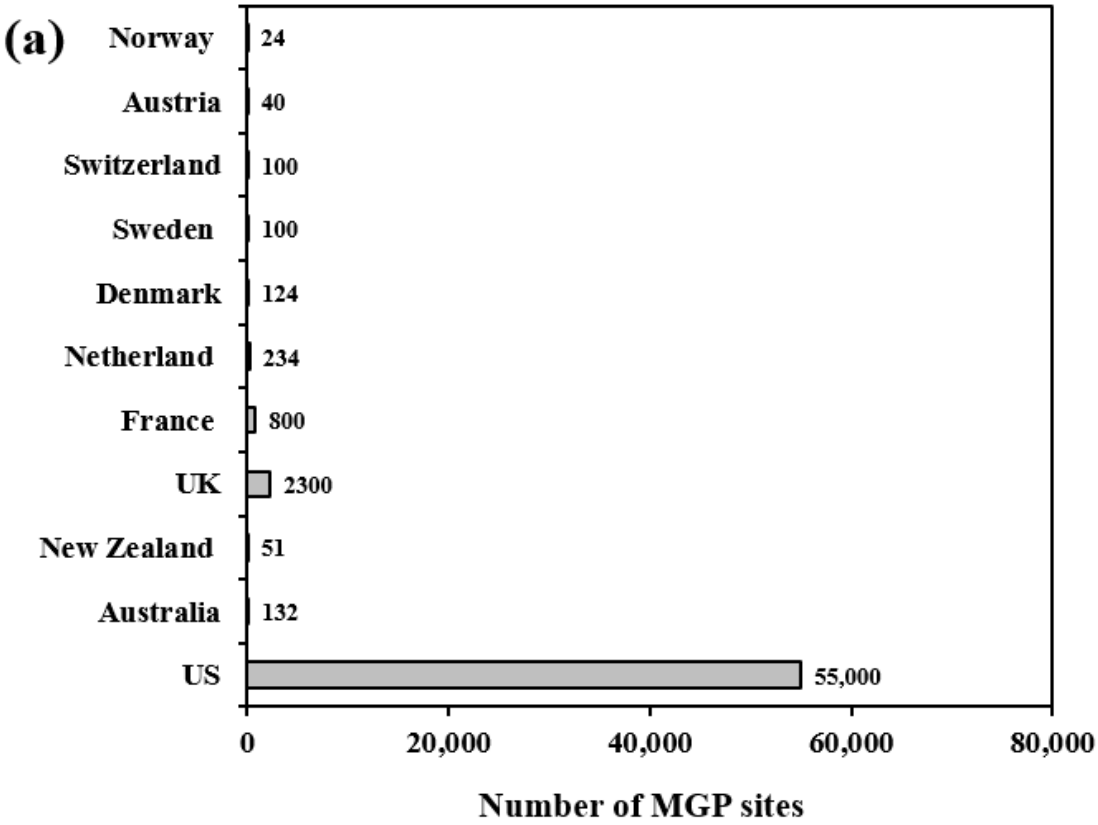


Fig. 2. MGP sites – (a) Global prevalence; (b) Current status of sites remediated at selected nations



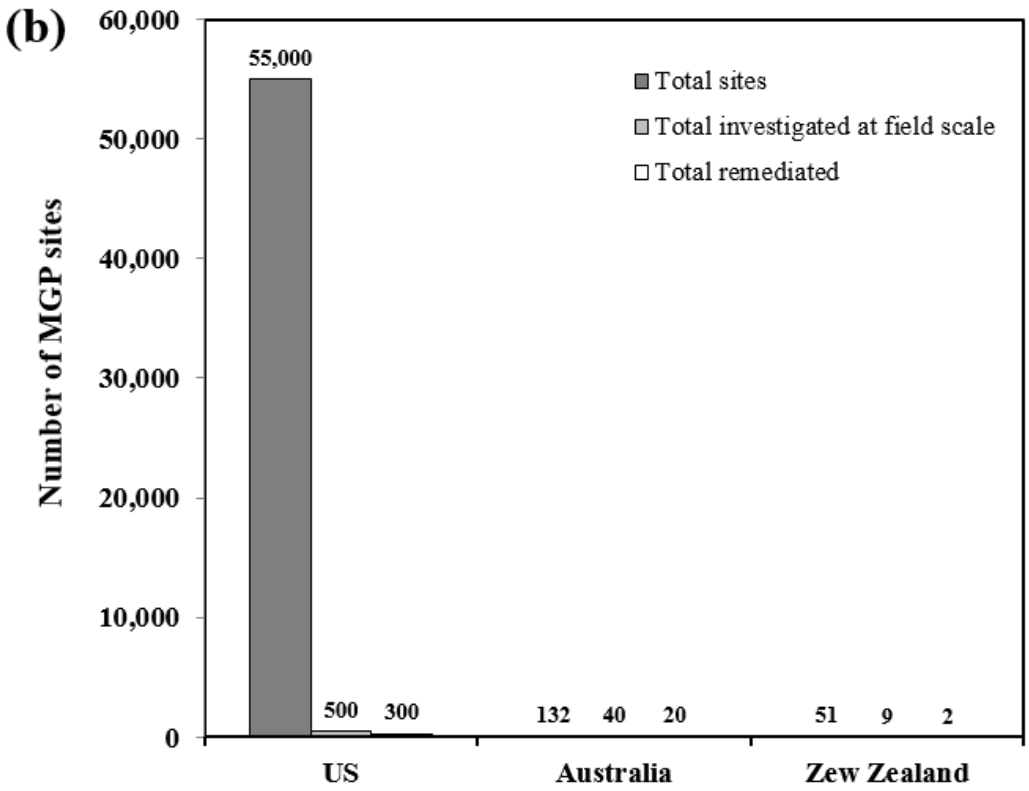


Fig. 3. Conceptual model – fate of PAHs in soil *vs* time

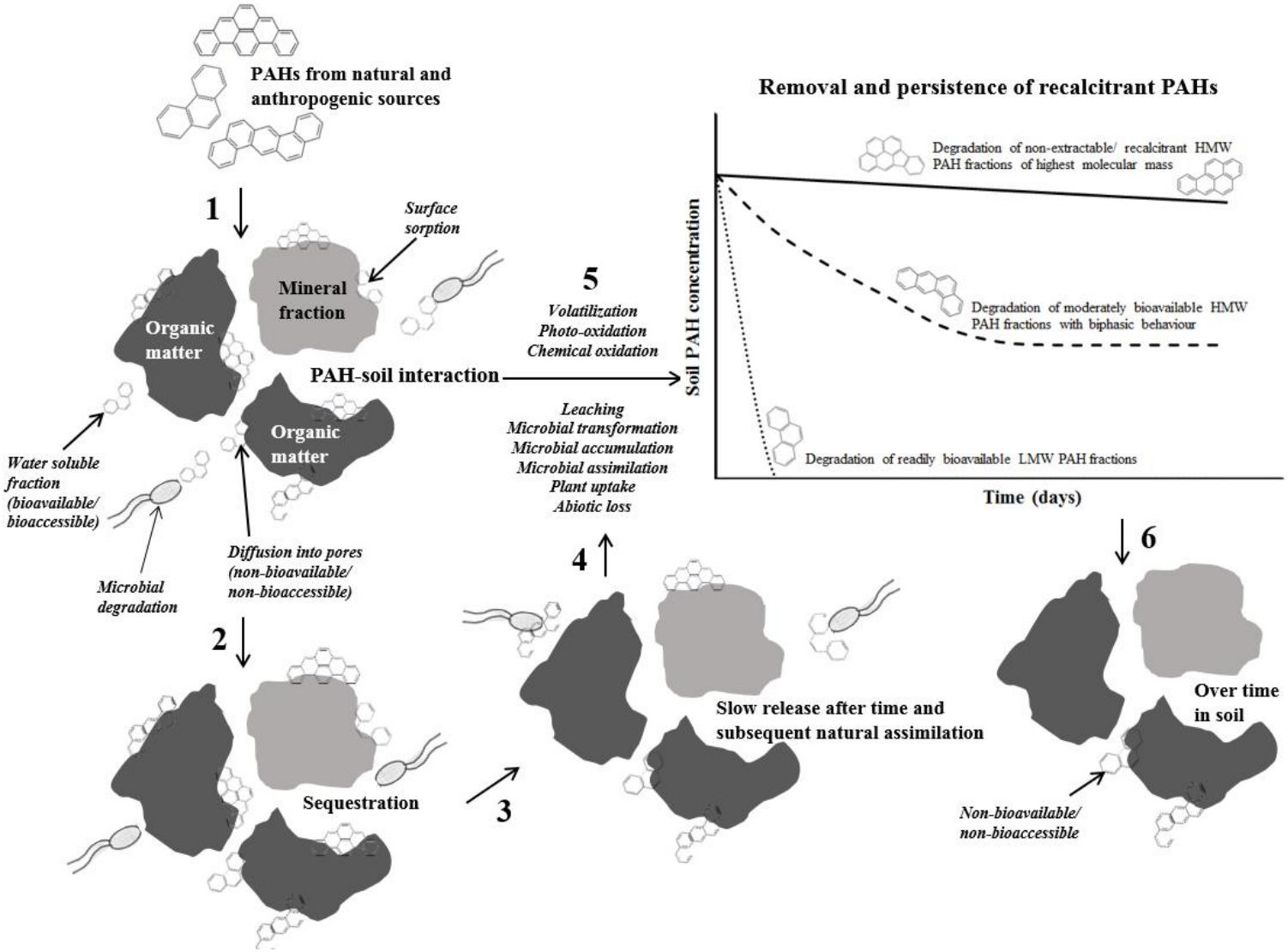
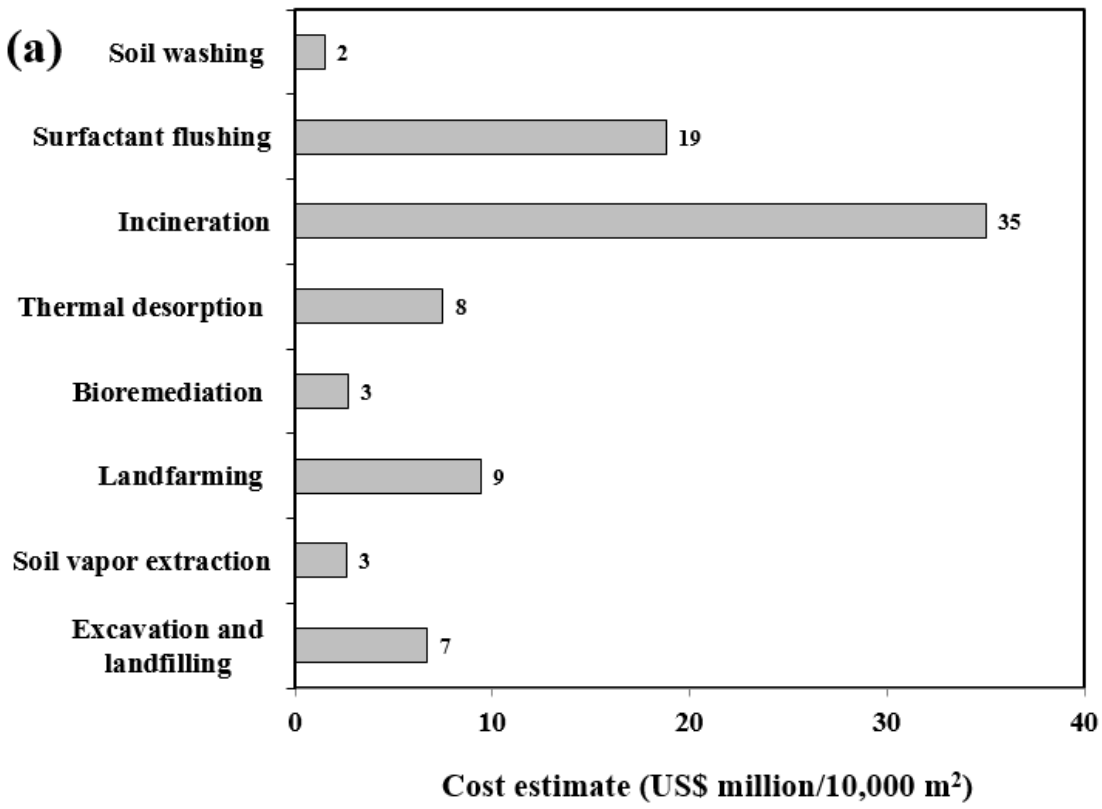


Fig. 4. MGP sites – (a) Cost estimate of technologies that are adopted by US EPA; (b) Breakdown (in %) of average remediation cost (in US$ million) by function



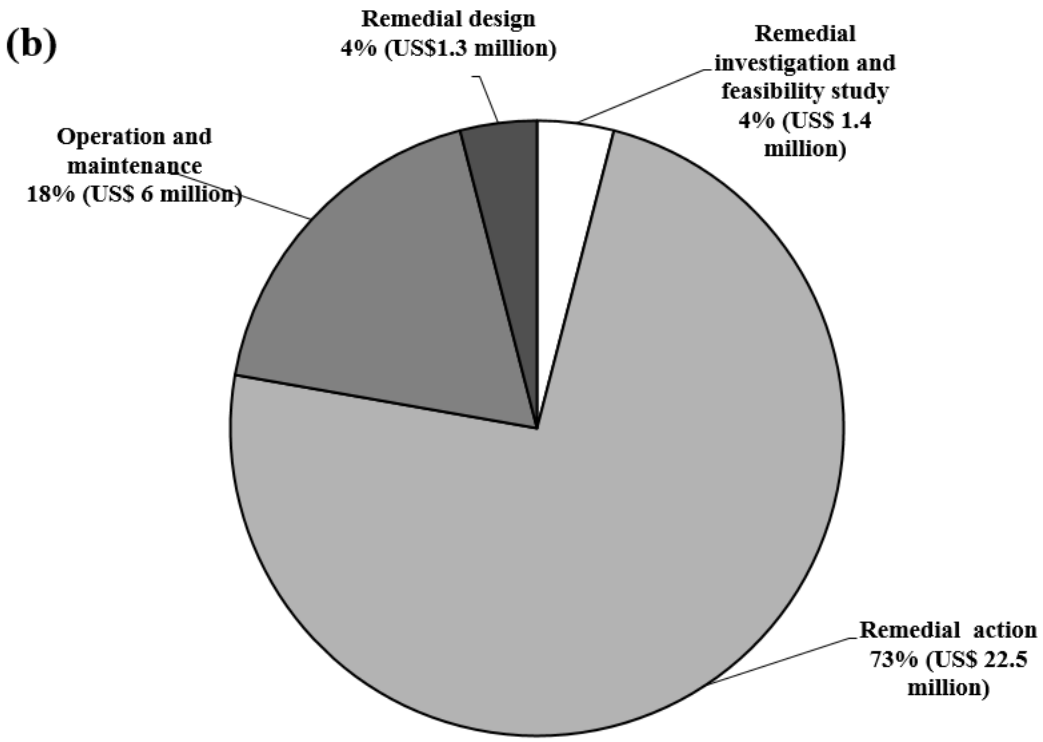
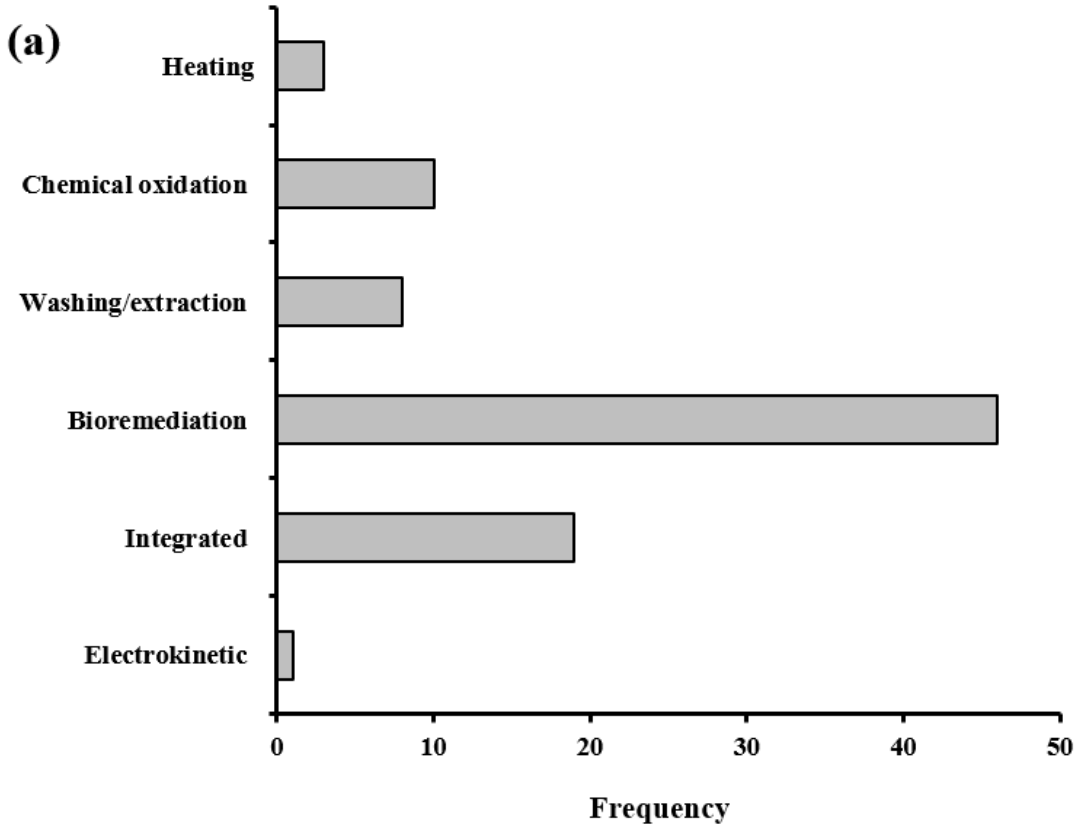
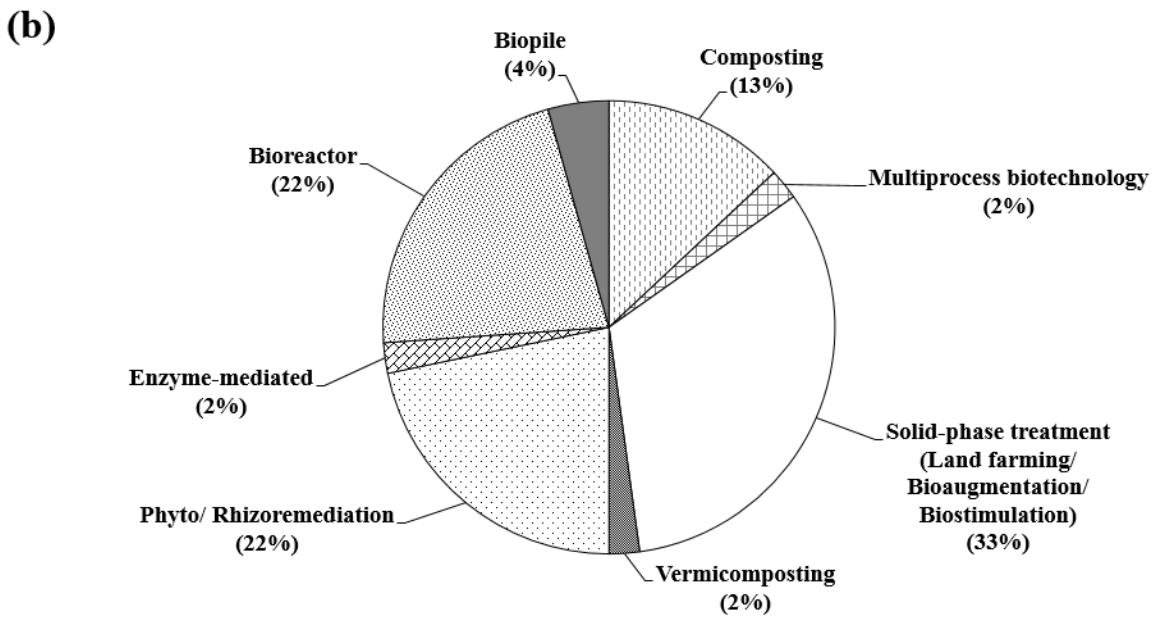


Fig. 5. Current trend – (a) Frequency of technology used in the remediation of PAH contaminated soils; (b) Bioremediation technologies used (in percentage terms) within its observed frequency range; (c) Integrated technologies use (in percentage terms) within its observed frequency range





(c)

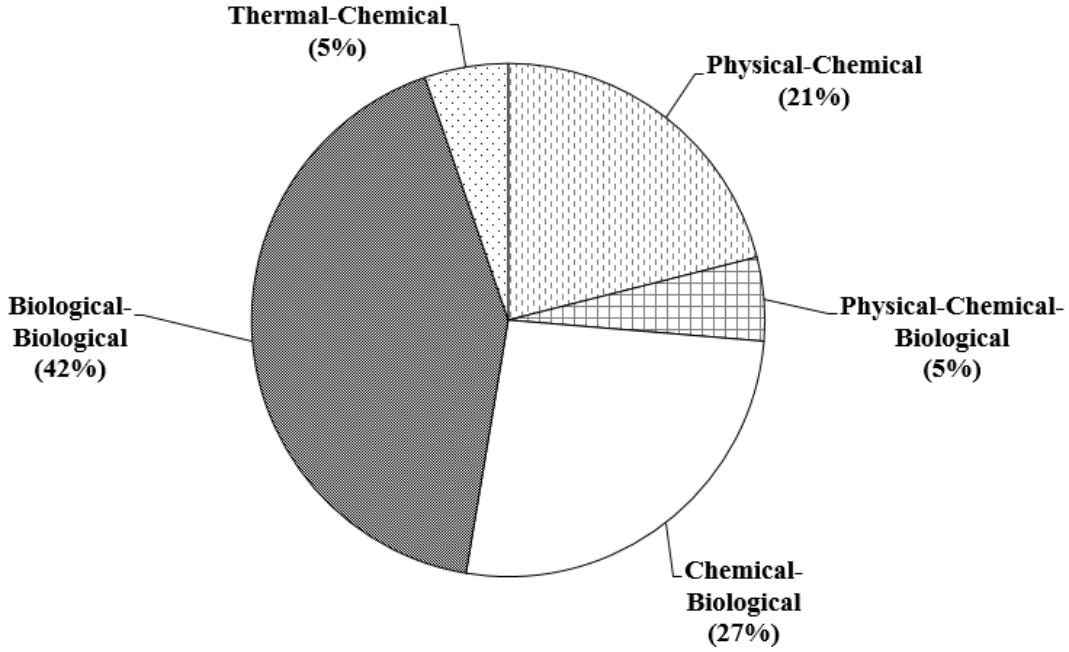

Thermal-Chemical
(5%)
Physical-Chemical
(21%)
Physical-Chemical-
Biological
(5%)
Chemical-
Biological
(27%)
Biological-
Biological
(42%)

Fig. 6. Factors affecting field-scale remediation of PAH contaminated soils

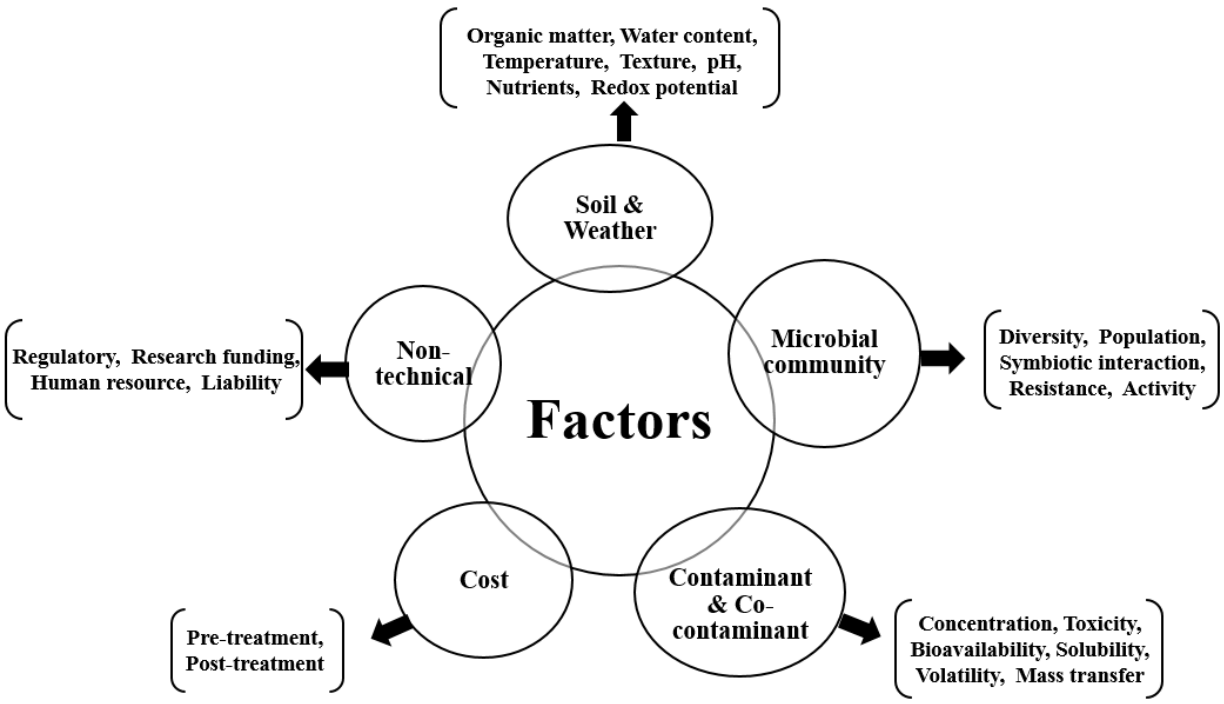


Table 1. PAH diagnostic ratio for the identification of soil pollution source

PAH ratio	Value range	Source
Phe/Ant	<10	Pyrogenic
	>15	Petrogenic
	2-8	Vehicle emission
Flt/Pyr	>1	Pyrogenic
	<1	Petrogenic
BaA/Chr	<2	Pyrogenic
	>2	Petrogenic
BaP/BghiP	>0.6	Traffic emission
BbF/BkF	2.5-3	Aluminium smelter emission
Ant/(Ant + Phe)	>0.1	Pyrogenic
	<0.1	Petrogenic
Flt/(Flt + Pyr)	>0.5	Pyrogenic
	<0.4	Petrogenic
	>0.5	Grass, wood, coal combustion
	0.4-0.5	Fossil fuel combustion
	1-1.4	Coal combustion
	<0.4	Gasoline, diesel engine
BaA/(BaA + Chr)	>0.35	Pyrogenic
	<0.2	Petrogenic
	>0.35	Combustion or vehicular emission
	0.2-0.35	Coal combustion
IcdP/(IcdP + BghiP)	>0.18	Pyrogenic
	<0.18	Petrogenic
	0.2-0.5	Petroleum combustion
	>0.5	Grass, wood, coal combustion
BaP/(BaP + Chr)	<0.3	Pyrogenic
	<0.3	Petrogenic
	0.07-0.24	Coal combustion
	0.3-0.7	Diesel engine
	0.49	Gasoline
Σ LMW PAH/Σ HMW PAH	<1	Pyrogenic
	>1	Petrogenic

Σ – Total/Sum; LMW – Low molecular weight; HMW – High molecular weight

Table 2. Extent of PAHs contamination in soils – industrial *vs* non-industrial

*No	PAH	Abbrev.	No of rings	$Half-life in soil (days)	Concentration of PAHs at contaminated sites (mg kg^{-1} soil)									
					Industrial area						Non-industrial area			
					FMGP site [d,l]	Coking plant [l,m]	Wood preserving [l]	Wood treatment [j,k,l]	Petrochemical plant [c,f]	Manufacturing site [h]	Residential		Roadside [b,e]	Forest [g]
											Rural [h,i]	Urban [a,c,e,f]		
1	Acenaphthene	Ace	3	102	2-222	50	7-1,368	0.1-100	0.002-0.02	0.4-0.6	0.003-0.2	0.001-0.1	0.004-0.5	0.003-0.1
2	Acenaphthylene	Acy	3	60	50-623		5-49	<0.5	0.002-0.01	0.2-0.7	0.002-0.1	0.002-0.02	0.001-0.04	0.005-0.02
3	Anthracene	Ant	3	50-460	55-295	6-130	10-3,037	0.1-766	0.002-0.05	0.07-0.2	0.002-0.02	0.004-0.04	0.006-0.2	0.0007-0.004
4	Fluorene	Flu	3	60	25-726	7-245		0.1-693	0.002-0.02	0.05-0.3	0.004-0.08	0.002-0.02	0.005-0.9	0.002-0.01
5	Phenanthrene	Phe	3	16-200	52-2,738	27-277	11-4,434	0.3-1,440	0.008-0.1	0.09-0.2	0.02-0.06	0.02-0.2	0.05-2.7	0.005-0.06
6	Benzo[a]anthracene	BaA	4	162-670	155-397	16-624	12-171	0.1-356	0.003-0.1	0.5-1.1	0.005-0.05	0.009-0.3	0.04-3.7	0.003-0.07
7	Chrysene	Chr	4	371-990	33-748	11-535	38-481	0.1-321	0.004-0.1	0.2-0.5	0.006-0.06	0.02-0.3	0.06-6.5	0.03-0.1
8	Fluoranthene	Flt	4	44-440	55-3,664	34-858	35-1,629	2.5-1,350	0.007-0.18	0.2-0.5	0.01-0.2	0.03-0.7	0.08-5.2	0.05-0.2
9	Dimethylbenz[a]anthracene	DbaA	4											
10	Methylcholanthrene	Mca	4											
11	Methylchrysene	Mc	4											
12	Nitropyrene	Np	4											
13	Pyrene	Pyr	4	199-1,870	55-1,245	28-578	49-1,303	0.4-983	0.02-0.2	0.3-0.5	0.01-0.06	0.03-0.6	0.08-3.2	0.006-0.02
14	Benzo[a]pyrene	BaP	5	229-530	58-738	14-502	28-82	0.1-93.7	0.005-0.1	0.5-1.3	0.009-0.1	0.02-0.3	0.04-5.5	0.005-0.08
15	Benzo[b]fluoranthene	BbF	5	67-610	108-552	260-645	38-140	0.1-6.5	0.007-0.04	0.3-0.5	0.02-0.2	0.002-0.5	0.05-8.8	0.01-0.1
16	Benzo[j]fluoranthene	BjF	5			238								
17	Benzo[k]fluoranthene	BkF	5	143-2,140	152-446	322		0.1-3.6	0.003-0.02	1.0-1.3	0.003-0.05	0.01-0.2	0.04-0.5	0.0009-0.06
18	Dibenz[a,h]acridine	DahAc	5											
19	Dibenz[a,j]acridine	DajAc	5											
20	Dibenzo[a,h]anthracene	DahA	5	361-940	950-3,836	125-2,450		10.1	0.002-0.01	1.5-2	0.008-0.02	0.006-0.05	0.008-9.2	0.01-0.08
21	Dibenzo[c,g]carbazole	DcgC	5											
22	Benzo[r,s,t]pentaphene	BrstP	6											
23	Dibenzo[a,e]fluoranthene	DaeF	6											
24	Dibenzo[a,e]pyrene	DaeP	6											
25	Dibenzo[a,h]pyrene	DahP	6											
26	Dibenzo[a,i]pyrene	DalP	6	232-361										
27	Indeno[1,2,3-cd]pyrene	IcdP	6	288-730	121-316	2-333	10-23	0.1-10	0.004-0.03	0.7-0.9	0.005-0.1	0.008-0.3	0.04-1	0.04
28	Benzo[g,h,i]perylene	BghiP	6	74-650		266		0.1-1.7	0.005-0.04	0.9-3.1	0.009-0.08	0.009-0.04	0.04-0.7	0.01-0.1
	Total PAHs				1,841-16,546	1,406-8,053	243-12,717	15-6,135	0.08-1	7-14	0.1-1	0.2-4	0.5-49	0.2-1

[*] PAHs numbered 1-28 are listed on the Toxic Release Inventory reported by US EPA National Waste Minimization Programme and US EPA Priority Chemicals list

[$]Biodegradation half-lives of PAHs in soil vary depending on the soil type and degradation conditions. The given half-life value of specific PAHs is an overall range reported in the literature, which do vary based on these two factors

FMGP – Former manufactured gas plant

Values are rounded to their nearest integer

[a] Zhang et al. (2006) - 0-10 cm depth soil ; [b] Bhupander et al. (2012) – depth of sampling not given; [c] Nadal et al. (2004) - upper 3cm soil; [d] Thavamani et al. (2012a) -1-50 cm depth soil; [e] Jiang et al. (2009) - 0-10 cm depth soil; [f] Nadal et al. (2009) - 0-5 cm depth soil; [g] Hu et al. (2006) - 0-10 cm depth soil; [h] Khillare et al. (2014) - 5 cm depth soil; [i] Maliszewska-Kordybach et al. (2013) - 0-30 cm depth soil; [j] Sabate et al. (2006) - depth of sampling not given; [k] Guerin (1999) - 30 cm depth soil; [l] Wilson and Jones (1993) - depth of sampling not given; [m] Smith et al. (2006) - 25 cm depth soil

Table 3. National soil quality guidelines for PAHs (mg kg^{-1})

Country/PAH	Land-use pattern				
	General	Agricultural	Residential	Commercial	Industrial
Canada [a]					
BaA		0.1	1	10	10
BkF		0.1	1	10	10
BaP		0.7	0.7	10	1.1
BbF		0.1	1	10	10
DahAc		0.1	1	10	10
BkF		0.1	1	10	10
IcdP		0.1	1	10	10
Phe		0.1	5	50	50
Pyr		0.1	10	100	100
Dutch [b]					
Total PAHs	40				
Australia [c,d]					
BaP	1 [d] (EIL)	1 [d] (HIL)	4 [d] (HIL)	2 [d] (HIL)	5 [d] (HIL)
Flu	10 [d] (EIL)				
Ant	10 [d] (EIL)				
Phe	10 [d] (EIL)				
Pyr	10 [d] (EIL)				
Total PAHs		300 [c] (HIL) 20 [d] (HIL)	400 [c] (HIL) 80 [d] (HIL)	300 [c] (HIL) 40 [d] (HIL)	4000 [c] (HIL) 100 [d] (HIL)
New Zealand [e]					
BaP		25	25	25	25
Pyr		160	1600		

[a] CCME (2010); [b] DTIV (2000); [c] NEPM (2013); [d] WADEP (2010); [e] NZME (2011); EIL - Ecological investigation levels; HIL - Health investigation levels

Table 4. Environmental and non-environmental workers for the remediation of contaminated site

Worker type	Site assessment	Remediation	Gross total
Non-environmental			
Equipment operator	200	1,650	1,850
General	180	450	630
Truck drivers	0	490	490
Total	380	2,590	2,970
Environmental			
Senior	30	130	160
Intermediate	50	260	310
Junior	210	900	1,110
Support	65	130	195
Total	355	1,420	1,775
Grand total (A + B)			4,745

Table 5. Potential of established and emerging technologies for treating PAHs contaminated field soils

Site	Technology description	Volume or area of soil treated	Initial PAH concentration (mg kg^{-1})	Operation duration (days)	PAHs studied	% PAH remediated	Study type	Reference
A. Thermal treatment – Incineration and thermal desorption[*]								
[b] Superfund, US	Incineration	142,000,000 kg	1,000	480	Nap, Ace, Acy, Flu, Phe, Ant, Flt, Pyr, BaA, Chr, BbF	90	F	Acharya and Ives (1994)
[a] Former wood treatment, US	Thermal desorption	29,800,000 kg	30.6	130	BaP	99.9	F	Baker et al. (2007)
[a] Lampblack residuals, US	Soil venting thermal desorption	70 kg	1,000	35	Nap, Phe, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, BghiP, IcdP	90	B	Hosseini (2006)
B. Physical treatment – Soil washing/ solvent extraction[*]								
[b] Bedford, UK	Soil washing with water and mixed organic solvents	1 g	11,600	1	Nap, Flu, Flt, Pyr, BbF, BkF, BaP, IcdP, BghiP	96.3	B	Khodadoust et al. (2000)
[b] 30 year old MGP, France	Extraction with cyclodextrin	50 g	655	7	Phe, Ant, Pyr	99	B	Viglianti et al. (2006)
[b] Former chemical plant, Italy	Soil washing with humic acid	10 g	4,560	1	Total PAHs (individuals not specified)	90	B	Conte et al. (2005)
[b] Gas plant, China	Soil washing with fatty acid methyl esters	5 g	997	2	Phe, Ant, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, BghiP, IcdP,	50-60	B	Gong et al. (2010)

					DahAc			
[b] MGP, China	Extraction with sunflower oil	150 g	5,453	7	Flu, Phe, Ant, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahA, BghiP, IcdP	81-100	B	Gong et al. (2005)
[b] MGP, Germany	Extraction with sunflower oil	1 kg	724 and 4,721	180	Flu, Phe, Ant, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahA, BghiP, IcdP	>90	B	Gong et al. (2006)
C. Chemical treatment – Chemical oxidation[*]								
[b] MGP, US	Oxidation with Fenton reagent	9 kg	1,164	40	Chr, BaA, BbF, BkF, BaP, IcdP, DahA	87-95	P	Pradhan et al. (1997)
[b] Coking plant, US	Oxidation with magnetite activated persulfate	1 g	1,300 and 1,400	7	Nap, Ace, Acy, Flu, Phe, Ant, Flt, Pyr, BaA, Chr, IcdP, BbF, BkF, BaP, DahA, BghiP	50-60	P	Usman et al. (2012)
[b] Former steel manufacture, France	Oxidation with $KMnO_4$	10 g	1,550	4	Nap, Ace, Acy, Flu, Phe, Ant, Flt, Pyr, BaA, Chr, IcdP, BbF, BkF, BaP, DahA, BghiP	70	B	Lemaire et al. (2013)
[b] MGP, US	Oxidation with iron activated persulfate	30 g	4,510	7	Nap, Ace, Acy, Flu, Ant, Phe, Pyr, Flt, Pyr, BaA, Chr, BaP, BbF, BkF, BghiP, IcdP, DahA	85-90	B	Killian et al. (2007)
[b] Superfund,	Oxidation with	5 g	2,000-3,000	1	Nap, Ace, Acy, Flu, Ant, Phe, Pyr, Flt,	50	B	Scott Alderman

US	peroxy-acid				Pyr, BaA, Chr, BaP, BbF, BkF, BghiP, IcdP, DahA			et al. (2007)
[b] Coking plant, France	Thermal pre-treatment and chemical oxidation	50 g	1,089 and 1,121		Nap, Ace, Acy, Flu, Ant, Phe, Pyr, Flt, Pyr, BaA, Chr, BaP, BbF, BkF, BghiP, IcdP, DahA	31-47	B	Usman et al. (2016)
D. Biological treatment – Solid-/ slurry-phase treatments, composting, biopiling, bioreactors and phytoremediation[*]								
[b] POPILE superfund, US	Open land farming units (tilling and nutrient addition)	0.46 m (depth) × 1.22 m (width) × 6.1 m (length)	13,000	730	Ace, Flu, Phe, Ant, Flt, Pyr, Chr, BaA, BbF, BbF, BaP	91-95	P	Hansen et al. (2004)
[a] Coke oven industry, Portugal	Land farming greenhouse unit (tilling and aeration)	100 m^2	1,140	150	Nap, Ace, Acy, Flu, Phe, Ant, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahAc, IcdP, BghiP	60	F	Picado et al. (2001)
[b] Shenfu irrigation area, China	Bioaugmentation with fungal consortium in solid- and slurry-phase	5 g	15.7	30	Ace, Acy, Nap, Ant, Flu, Phe, Chr, Flt, Pyr, BaA, BaP, BbF, BkF, DahP, BghiP, IcdP	45-56	B	Li et al. (2008)
[b] Gas and wood treatment plants, Czech Republic	Bioaugmentation with fungi	5 g	2,320 and 612	42	Nap, Ace, Acy, Flu, Phe, Ant, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahAc, IcdP, BghiP	58-73	B	Leonardi et al. (2007)

[b] Industrial, Italy	Slurry- and semisolid-phase aerobic bioreactors	26 kg	3,700	35	Nap, Ace, Flu, Phe, Ant, Flu, Pyr, BaA, Chr	60-70	B	Pinelli et al. (1997)
[b] Landfill, Italy	Slurry-phase aerobic bioreactor in the presence of autochthonous bacterial strains and surfactant	150 g	70.4	30	Nap, Ace, Acy, Flu, Phe, Ant, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahAc, IcdP, BghiP	60	B	Ginnaro et al. (2008)
[b] MGP, Australia	Bioaugmentation of heavy metal tolerant PAH degrading bacterial consortium	5 g	889	60	Nap, Ace, Acy, Flu, Phe, Ant, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahAc, IcdP, BghiP	40-50	B	Thavamani et al. (2012)
[b] MGP, Australia	Bioaugmentation of acid-heavy metal-tolerant PAH degrading N-fixing and P-solubilizing bacterial consortium	0.5 kg	3967	105	Ace, Phe, Ant, Flt, Pyr, BaA, BkF	40-90	B	Kuppusamy et al. (2016b)
[b] Creosote treatment plant, US	Static pile compost system with poultry manure	350 kg	1,086.9	570	Nap, Ant, Phe, Flu, Pyr, Chr, Flt, BaP	98	B	Atagana (2004)
[b] Gas work plant, Czech Republic	Thermally insulated composting with mushroom compost	170 kg	610	100	Phe, Ant, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahA, BghiP, IcdP	37-80	B	Sasek et al. (2003)
[a] Gas work plant,	Composting	1-1.5 kg	6,915	210	Nap, Ace, Acy, Flu, Phe, Flt, Pyr, BaA,	50-90	F	Guerin (2000)

Australia					Chr, BbF, BkF, BaP, DahA, IcdP, BghiP			
[a] Industrial channel, Italy	Composting in reactor	146 kg	200	130	Nap, Ace, Acy, Flu, Phe, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahA, IcdP, BghiP	68	P	Moretto et al. (2005)
[a] Oil refinery, Serbia	Biopile	2.7 m3	3.6	500	Nap, Ace, Acy, Flu, Phe, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahA, IcdP, BghiP	77	F	Maletic et al. (2009)
[a] Agricultural land adjacent to an iron and steel foundry, China	Intercropping with tall fescue (*Festuca arundinacea*) and alfalfa (*Medicago sativa*)	12 plots each of 1.6 x 2.2 m	747-810	210	Nap, Ace, Acy, Flu, Phe, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahA, IcdP, BghiP	31	F	Sun et al. (2011)
[b] Coke plant, China	Phytoremediation with multispecies (ryegrass – *Lolium perenne*, white clover – *Trifolium repens* and celery – *Apium graveolens*)	1 kg	23.1	75	Nap, Ace, Acy, Flu, Phe, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahA, IcdP, BghiP	52	G	Meng et al. (2011)
[b] Creosote contaminated, Canada	PGPR assisted phytoremediation using wild rye	1.2 kg	500-3,000	120	Nap, Ace, Acy, Flu, Phe, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahA, IcdP, BghiP	90	B	Huang et al. (2004)
[b] Agricultural	Microbe assisted phytoremediation by	1.5 kg	10.1	90	Nap, Ace, Acy, Flu, Phe, Flt, Pyr, BaA,	51	G	Teng et al. (2011)

land, China	alfalfa				Chr, BbF, BkF, BaP, DahA, IcdP, BghiP			
[b] Long-term contaminated locality, Germany	Enhanced phytoremediation using ryegrass	5 kg	355.9	540	Nap, Ace, Flu, Phe, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahA, IcdP, BghiP	50	G	Resek et al. (2008)
E. Integrated approaches – physical-chemical, biological-physical, biological-chemical, physical-chemical-biological and coupled biological strategies [*,^]								
[b] Former MGP, US	Pre-treatment with vegetable oils (corn or palm kernel) prior to treatment with Fenton's oxidation	10 g	3,100 and 7,700	14	Flu, Phe, Ant, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DaA, BghiP, IcdP	20-49	B	Bogan et al. (2003)
[b] MGP, Sweden	Ethanol desorption prior to Fenton's oxidation	20 g	1,567	1	Nap, Ace, Acy, Flu, Phe, Ant, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahA, IcdP, BghiP	16-40	B	Lundstedt et al. (2006)
[b] Creosote contaminated clay, Finland	Electrokinetically enhanced oxidation with sodium persulfate	2.3 kg	420	56	Nap, Ace, Acy, Flu, Phe, Ant, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahA, IcdP, BghiP	35	B	Isosaari et al. (2007)
[b] Coal-tar contaminated, US	Solvent (ethanol or acetone) pretreatment followed by slurry-phase bioremediation	200 g	1,500	35	Nap, Ace, Acy, Flu, Phe, Ant, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahA, IcdP, BghiP	90	B	Lee et al. (2001)
[a,b] MGP, US	Initial aerobic treatment with	1-2 kg (B) 16 plots each	35,000	70	Nap, Ace, Acy, Flu, Phe, Ant, Flt, Pyr,	98 (B) 50 (F)	B, F	Srivastava et al. (1994)

	Fenton's oxidation as a post-treatment followed by a second round of biological treatment (B) Chemical oxidation using Fenton's reagent as pre-treatment followed by biological treatment using an aerobic biosystem (F)	of 0.1 x 0.3 m (F)			BaA, Chr, BbF, BkF, BaP, DahA, IcdP, BghiP			
[b] Industrial, Italy	Slurry bioreactor combined with ozone oxidation	0.75-1.5 kg	10.2	280	Nap, Ace, Phe, Ant, Flt, Pyr, BaP	80	B	Derudi et al. (2007)
[b] Wood impregnation plant, Belgium	Combination of modified Fenton and biodegradation	1.25 kg	3,318	112	Phe, Ant, Flu, Nap	40-60	B	Palmroth et al. (2006)
[b] Wood impregnation plant, Finland	Initial soil washing with water followed by ozonation and final biological treatment using Pseudomonas strain and nutrients	1 kg (B) 25 kg (P)	1,200	12	Nap, Ace, Acy, Flu, Phe, Ant, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahA, IcdP, BghiP	90	B, P	Haapea and Tuhkanen (2006)
[b] Oil treatment plant, Mexico	Enhanced system of biostimulation-bioaugmentation with filamentous fungi	10 g	7,560	35	Nap, Ace, Phe, Ant, Flt, Pyr, Chr, BkF, BaP, IcdP	50-70	B	Mancera-Lopez et al. (2008)
[b] MGP, US	Phytoremediation as a secondary treatment	2.1 kg	-	365	Nap, Ace, Acy, Flu, Phe, Ant, Flt, Pyr,	10-24	G	Parrish et al.

	of a soil subjected to ex-situ composting/biopiling				BaA, Chr, BbF, BkF, BaP, IcdP, BghiP			(2004)
[b] Former wood treatment facility, US	Landfarming with bioaugmentation and biostimulation	-	13,000	480	Ace, Flu, Phe, Ant, Flt, Pyr, BaA, Chr, BbF, BkF, BaP	87	B, P	Straube et al. (2003)
[b] Farm, Canada	Multiprocess phytoremediation system – land faming + bioaugmentation + phytoremediation	1 kg	500-3,000	120	Nap, Ace, Acy, Flu, Phe, Ant, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahA, IcdP, BghiP	55-80	B	Huang et al. (2004)
F. Others [^]								
[b] MGP, US	Electrokinetic remediation	1.2 kg	720	23	Nap, Ace, Flu, Phe, Ant, Flt, Pyr, BaP, Chr, BbF, BjF, BkF, IcdP, DahA, BghiP	94	B	Maini et al. (2000)
[b] Gas work, Australia	Vermiremediation	5 kg	11,820	84	BaA, Chr, BbF, BkF, BaP, DahP, BghiP	70-90	B	Sinha et al. (2008)
[b] Petroleum gas station, China	Laccase enzyme mediated biodegradation in the presence of a redox mediator	3 g	0.5	14	Nap, Ace, Flu, Phe, Flt, Pyr, BaA, Chr, BbF, BkF, BaP, DahA, IcdP, BghiP	20-80	B	Wu et al. (2008)

[a]In-situ; [b]Ex-situ; [*]Established technology; [^]Emerging technology; B - Bench-scale; P - Pilot-scale; G - Greenhouse study, F - Field-scale