Assessment of PAH contaminated land: Implementing a risk-based approach

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Highlights

- Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment
- Land use alter the composition and fate of PAHs
- Risk based corrective action abate threats caused by carcinogenic PAHs
- Bioaccessibility should be implemented in risk assessment of PAHs
- Specific biochar can be used to mitigate risks

Graphical Abstract

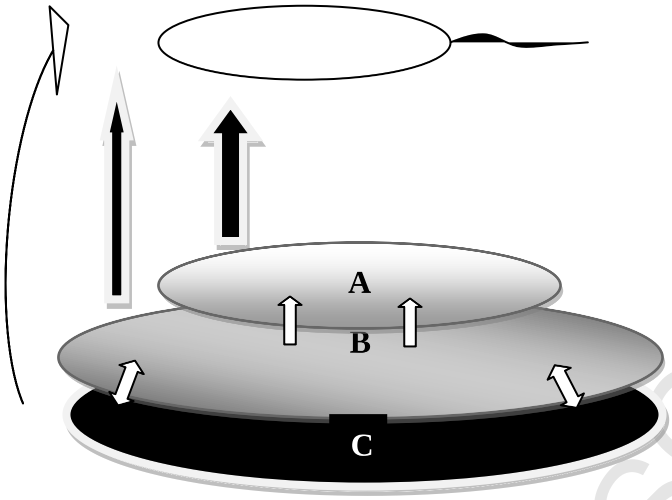

Figure 3 Bioaccessibility of PAHs in soil where A, B and C represent the bioavailable, bioaccessible and non-bioaccessible fractions, respectively (Adopted from Ogbonnaya and Semple, [72])

Assessment of PAH contaminated land: Implementing a risk-based approach

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are amongst the most common ubiquitous anthropogenic pollutants of terrestrial ecosystems. There are currently multiple sources of PAHs in Nigeria and land use activities have been shown to alter the composition of PAHs and in some cases increase the fractions of carcinogenic and recalcitrant components. This report considers the implementation of a more specific risk based corrective action to abate threats caused by carcinogenic PAHs in eroded and degraded soils for prospective risk assessment and realistic decision-making. Bioremediation is promoted for degradation of PAHs in soils, but faces several limitations that question the effectiveness of the approach. This review provides insights into bioaccessibility and chemical activity assessment of PAHs as a procedure of risk assessment and the potential use of specially produced biochar designed for specific risk mitigation remedial action was also considered.

Keywords: Bioaccessibility; c-PAHs; mitigation; risk; remediation; chemical activity

Introduction

Contaminated land is a critical issue and of great public health and environmental concern internationally. Extensive activities such as the exploration, production, transportation, storage and use of crude oil and its petroleum derived products which has several footprints within the environment, despite implementation of preventive measures. In Nigeria, the oil and gas industry under the auspices of the Department of Petroleum Resources (DPR), Environmental Guidelines and Standards of the Petroleum Industry in Nigeria (EGASPIN) was initiated and issued in 1991 and revised 2002 to ensure control of petroleum hydrocarbon pollution in the environment associated with the operations of Petroleum industry. Similarly, the National Oil Spill Detection and Response Agency (NOSDRA) which was initiated in 2006 and assumed the responsibility of detection, monitoring and remediation but may not cover supervision of remediation activity.

The frequent exploration, production, transportation, storage and use of crude oil and its derivatives leave several environmental footprints within the Nigerian land and receiving coastal environment. Despite implementation of waste management strategies during exploration and production, rapid detection and response to spills, several historical and newly contaminated sites require remediation and are currently posing severe life threatening hazards to humans and biota likewise. The challenges to effective remediation of such sites are attributed to: overlap of responsibilities of agencies, limited resources for agency operations, conflict of interest, shortage of knowledgeable technical personnel, transparency, security risk, cost, inadequate regulatory requirements and enforcement, interpretation of EGASPIN and inaccessibility to legislation (EGASPIN), site accessibility and land use [1,2]. Although the agencies and operators are seeking approaches to tackle these challenges, the mode of approach seems ambiguous.

EGASPIN recommends the use of the Risk-Based Corrective Action (RBCA) often referred to as “Rebecca” approach for contaminated land remediation, considering an intervention value of 5,000 mg kg^{-1} for mineral oil which is oftentimes referred to as total petroleum hydrocarbons (TPH). Historically, TPH has usually been the main criterion for environmental management of oil and gas operational locations internationally, owing to the development of acceptable health risk-based TPH levels [3]. Chemicals of critical concern such as polycyclic aromatic hydrocarbons (PAHs) and heavy metals found in crude oil and their derivatives are often in low concentrations, potentially posing a low risk to receptors [3-5]. This does not rule out that the ambiguous TPH measurement alone can either be under or over protective to receptors, since petroleum chemical composition and properties can vary from site to site. In addition, TPH measurement does not take into account the land-use where oil and gas facility is located, method of spill (vandalisation of pipelines or explosion), illegal refining (still on-going), blow out of abandoned oil wells and the destruction of petroleum products found by security operatives in Nigeria. These activities often alter the nature and composition of crude oil and its derivatives, which can significantly increase the level of specific concerned contaminants.

The constituents of TPH include::alkanes, alkylated alkenes, cyclic alkanes, phenols, organosulphur and organonitrogen compounds, acids, alkynes, alkyl benzenes and PAHs [5]. The consequences of releasing such compounds are far reaching since petroleum hydrocarbons together with heavy metals (lead, iron, cadmium, nickel) are released into the environment, thus contaminating the air, surface and ground waters, sediments, soils, vegetation and organisms. In some instances, there have been reported cases of fire outbreak due to such activities, hence, the regulatory system and policy for contaminated land remediation requires a more systematic approach considering chemical indicators and fractions in risk assessments. Hence, DPR initiated the intervention and target values for petroleum contaminants as protective and remedial endpoints for site assessment and remediation. The intervention value indicates quality for which the functionality of soil for human, animal and plant life are being threatened or seriously impaired with concentrations $\geq$ 5,000 mg kg^{-1} and $\geq$ 40 mg kg^{-1} for TPH (mineral oil) and PAHs, respectively [6]. The target value indicates soil quality required for sustainability in terms of remedial policy, the soil quality required for full restoration of soil's functionality for human, animal and plant life which is 50 mg kg^{-1} and 1 mg kg^{-1} for TPH (mineral oil) and PAH, respectively. Thus, this is the soil quality aimed for as requested by DPR [6]. A major weakness of the Nigerian standard is that where there is relative high risk of contaminant exposure and presence of carcinogenic PAHs at concentrations below the intervention values, no action is required to be taken. In contrast, the Dutch Environmental Standards considers levels below the intervention value where there is obvious human exposure. In addition, more emphasis is paid to TPH remediation without considering the risk posed by specific persistent and toxic contaminants present in the TPH continuum or generated during land-use.

PAHs are a class of organic contaminants dispersed into the environment through incomplete combustion of organic materials and by natural processes [7,8]. PAHs are composed of two or more fused aromatic rings in linear or clustered arrangements containing carbon and hydrogen atoms with nitrogen, sulphur, and oxygen atoms substituted with the benzene ring to form heterocyclic aromatic compounds [9]. They are dominantly lipophilic in nature and have been classified into two subgroups which are the low molecular weights (LMW) (two or three fused rings) and high molecular weights (HMW) (four or more fused rings) (Figure 1). Majority of PAHs are considered to be low in concentrations but pose more toxic and recalcitrance under normal conditions, hence, total TPH concentration as a tool for risk-based approach to remediate all hydrocarbon polluted site therefore has limited benefits. This paper promotes the implementation of specific chemical risk-based assessment of petroleum contaminated sites based on land properties, land-use and method of spill. It also considers the differences in soil within Nigeria, which affects the fate and transport of PAHs in the soil environment.

2.0 Production of polycyclic aromatic hydrocarbons

PAHs have been of growing concern due to consistent release, persistence, toxicity and transport. Most of the inputs are anthropogenic and thus can be controlled by avoidance, minimisation, recovery or treatment. The major sources of anthropogenic inputs into the environment are: automobile fuel combustion, pyrolytic processes, waste incinerators, domestic heaters, spillage of petroleum products, creosote wood treatment facilities, gas stations, sewage discharge and waste dumping, cigarette smoking, barbeque and roasting food, shipping and boating activities [10-14]. Thus, PAHs are ubiquitous as they can be found in soils, sediment, water and air particulates, with a potential of human exposure through the atmosphere, food and soil contact [15-17]. They are highly recalcitrant molecules, especially when they are HMWs and can cause carcinogenic, mutagenic, kidney and liver damages in humans [18]. Their formation can vary with substrate, fuel type and actual pyrolysis conditions [19-21].

In detail, during combustion of light hydrocarbons such as acetylene and methane, several radicals are produced in the gas phase, and the combination of propargyl radicals (C_3H_3) lead to the formation of benzene [19,22,23]. Propargyl and acetylene (C_2H_2) can also react to produce cyclopentadienyl radicals (C_5H_5) [21] or two step hydrogen abstraction and acetylene addition (HACA) mechanism on benzene produces naphthalene [19,21].

Alternatively, the cyclopentadienyl radical can undergo radical recombination to form naphthalene with loss of hydrogen [24-26]. Following benzene pyrolysis, aromatic growth is initiated to form biphenyl, which in the presence of acetylene forms phenanthrene [21]. Subsequently, HACA mechanism on lower molecular weight (LMW) PAHs, such as naphthalene and phenanthrene occurs where hydrogen abstraction creates a surface radical, acetylene addition to the radical formed and followed by ring cyclisation leads to the formation of higher molecular weight (HMW) PAHs [21,25,27]. Alternatively, reaction of the phenyl ring with a PAH accompanied by acetylene addition and dehydrocyclisation produces a five-membered ring PAH [28]. Increasing time and temperature of combustion leads to increasing yields of all PAHs, especially the three-, four- and five-ring PAHs, accompanied by the formation of numerous methyl and phenyl substituted PAHs [20]. This is an obvious situation that occurs within the Niger Delta region of Nigeria where illegal refining activity occurs (artisanal refining), destruction of petroleum products, blow out of production wells or any condition where combustion of fossil fuel occurs. When these compounds are dispersed into the environment, they are mainly deposited through wet or dry deposition onto soil via point or diffuse sources [13,29]. The concentrations of PAHs within the soil vary, due to proximity to source, environmental conditions and properties of media in which it is found [16,30]. LMW PAHs can also exist in more complex mixtures as creosote, soot and coal tars [20,21,31], When LMW PAHs are more dominant (60-70%), it is suggested that the source of PAHs is fresh liquid spill, whereas when HMW PAHs are more abundant, it is suggested that the source is of pyrogenic origin [11,32].

2.1 Behaviour of PAHs in the soil environment

Detailed information is available in literature on the fate of PAHs in soil [33,34]. Briefly, when PAHs gain access to soil, fractions may be lost through volatilisation, leaching, or degradation at varying rates and extents due to differences in PAH physic-chemical properties and soil characteristics [35-39]. These processes (volatilisation, leaching and degradation) remove the mobile fractions, bioavailable and rapidly desorbable fractions of PAHs from soils leaving residual fractions that subsequently persist for a longer period of time [36,40,41] (Figure 2). However, microbial degradation of organic contaminants, such as PAHs stand out as the major mechanism for their removal, hence this process has often been favoured, stimulated and implemented in remediation of contaminated land globally.

The biodegradation of a PAH is hence limited to intrinsic properties, soil properties, indigenous microbial population, chemical toxicity and environmental conditions. Hence, a highly toxic and recalcitrant PAH like benzo (a) pyrene (B[a]P) can readily be sorbed into the soil matrix (SOM, clay) thereby reducing its bioaccessible fraction to microorganisms [38]. The residual or non-bioaccessible fractions of PAHs also implies it is poorly available to organisms and could hence be considered as being inert and pose less risk following proper management. However, if the soil texture does not favour sorption of such contaminant, fractions of the parent compound and the metabolites pose considerable risk to receptors [42,43].

2.2 Soil Texture and Conditions

The soil texture varies greatly in different areas of Southern Nigeria where majority of oil exploration activities occur (Table 1). In addition to the inherent physical properties of the soils, the soils within southern Nigeria are in areas of high rainfall exceeding 2,000 mm with high intensities, high erositivity and undulating topography [44-46]. Land or soil degradation associated with wind and water erosion in Sub Sahara Africa has been extensively reported [47-49]. Although Table 1 does not give a total overview and variation of all the soils in southern Nigeria, it however gives an insight on the very-degraded and vulnerable soils (low SOM and clay content) reported in literature. This is due to high temperatures, continuous cultivation and frequent burning of vegetation on land [46]. In confirmation, the United Nations Environment Programme [56] reported southern Nigeria as a location with potentially and very-degraded soils. For instance, the soils in Oyo were either poorly or imperfectly drained inland valleys which would have collected most of the minerals from eroded upland soils following runoff (Table 2). Such inland valleys are low to erosion and characterised with high silt and clay content. Soils in Ekiti, Kogi and Rivers states had SOM content $\leq$ 3% and Rivers state (oil-rich region) had clay content below 2%. However, the soils located in the swampy areas of mangrove tidal flat area of Niger Delta are associated with fine, organic and very poorly drained high silt and clay content (40-97%) [57]. In petroleum-contaminated areas, Okoro et al. [54] discovered very high concentrations of OM within soil and such OM content was attributed to aged decomposition of TPH. This was due to application of bioremediation approach (33 months) on the contaminated land by the company responsible and presence of grease. Similarly, Ujowundu et al. [53] observed higher SOM content in diesel contaminated soil, owing to the high level of petroleum contamination. This suggests that such SOM was mainly composed of petroleum hydrocarbons which would not contain required micronutrients for plant optimum growth and ecosystem sustainability. Rather, it contains potentially toxic compounds that would pose significant harm in future when released via SOM biotic and abiotic degradation.

2.3 TPH and PAH contaminated soils in Nigeria

Following the establishment of NOSDRA, over 9,200 oil spills were reported between January 2006 and 2015. More recently, over 3,222 spills have been reported since January 2013 despite reduced oil exploration and production activities [58,59]. Majority of the major oil spills were reported to be due to artisanal activities, sabotage by bursting of delivery pipes and theft of unrefined or refined oil at various quantities. Spills of smaller amounts have been due to aged pipes, equipment failure, natural incident, accident and maintenance error [2,59]. The composition of the spills however differs due to source, process of spill event and remediation process. For instance Ezenne et al. [60] showed that composition of TPH and PAH can differ in concentration despite having same source owing to different processing in soils. Most site assessment studies in Nigeria have focused on TPH concentration, without considering PAH fractions which constitute more toxic and persistent contaminants. For instance, following oil spills over 15 years ago in a community where oil and gas exploration activities took place in Rivers State, Nigeria, soil samples were collected at various depths and homogenised [61]. At the two most contaminated sites, mean TPH concentration ranged from 101 mg kg^{-1} to 1,651 mg kg^{-1}, with groundwater concentration exceeding 12,000 mg kg^{-1}. Although the authors did not provide information on the mode of spillage, it shows that groundwater can be contaminated by leaching, depending on the properties of soil and persistence of spillage. Okop and Ekpo [62] also showed that soil samples around a well head of an oil pipeline contained TPH levels between 54 mg kg^{-1} and 345 mg kg^{-1}. This was due to spillage of crude oil from the aged facility.

Similarly, soil samples were collected around a depot facility carrying refined petroleum products in Aba, Abia state Nigeria at three different depths (0-10, 10-20, 20-30 cm). The concentrations of TPH ranged from 5,120 mg kg^{-1} (20-30 cm depth) to 24,900 mg kg^{-1} (0-10 cm depth) [63], whilst a control site had less than 1 m kg^{-1} TPH concentration. The author observed that total PAH concentration did not exceed 1% of the value of TPH concentration at each depth but it exceeded the PAH concentration at control site. This showed that the spill of oil within the site may be due to corrosive pipes or tanks and the low PAH fraction would have been part of the TPH in the refined product. Similarly, soil samples collected from diesel storage sites located in Imo state recorded 46,726 mg kg^{-1} and 844 mg kg^{-1} of TPH and PAH, respectively, showing the presence of PAH in diesel oil [53]. Although below 2% of TPH, the high PAH concentration was due to aging of the contaminant within the soil around the storage site. More recently, Okpashi et al. [64] determined the TPH and total PAH concentration in soils following crude oil overflow by a flow-station owned by an oil company located in Delta state, Nigeria. The authors found 15,056 mg kg^{-1} and 2,462 mg kg^{-1} of TPH and PAHs, respectively present in the soils.

Over thirty years ago, an undisclosed quantity of crude oil spilled from an unknown source around Ejamah Ebubu in Eleme Local Government area of Rivers State, where a pipeline running inside the town existed [65]. The spill flowed along the topographic slope, contaminating the soils and surface waters and the crude oil ignited and burned for several days before the fire was brought under control. The concentrations of TPH and the associated benzene, toluene, ethylene and xylene (BTEX) and PAH fractions within the swamp sediment were investigated. Results showed that TPH ranged from 14.6 mg kg^{-1} to 28,687 mg kg^{-1} with an average value of 4,979 mg kg^{-1}, BTEX values did not exceed 0.1 mg kg^{-1} and PAH values ranged from 8.42 mg kg^{-1} to 14,130 mg kg^{-1} with an average value of 2,517 mg kg^{-1} [65]. In another study by Mmom and Deekor [57], well-drained and water-logged acidic soils within the mangrove area inhabiting oil exploration activities, had varying concentrations of TPH and PAH with minimal BTEX. TPH concentrations ranged between 3,100 mg kg^{-1} and 6,600 mg kg^{-1}, whilst PAH fractions ranged between 2,100 mg kg^{-1} and 4,100 mg kg^{-1}. Interestingly, PAH fractions ranged from 46% to 86% of the value of TPH which indicates a remarkable proportion suggesting most of the sites had experienced ignition thereby raising PAH concentrations. The authors implemented a land farming (bioremediation) approach to degrade the petroleum contaminants but this failed to ensure the concentrations of PAHs go below 1,268 mg kg^{-1}. In fact, a maximum of approximately 50% of total PAHs was biodegraded, owing to the acidic nature, water logging of soil and toxicity of the PAHs.

Based on the above studies, although TPH may be reduced to values permissible by the regulatory bodies through biodegradation, contaminated soils can still exhibit highly toxic characteristics due to the PAH concentrations within. Stroud et al. [38] demonstrated rapid removal of aliphatic hydrocarbon followed by the PAHs, with the HMW PAHs (pyrene, B[a]P) being more persistent having low catabolic potential. The concentration of inherent PAHs in petroleum products may be sufficiently low, but when hazardous events associated with elevated temperatures occur (explosions, fire outbreak, ignition or bush burning), increases in PAH concentration occurs, hence increasing the toxic conditions. As previously indicated in this current paper, most of the soils within southern Nigeria region exhibit low OM content and clay (vulnerable and degraded soils), reducing PAH sorptive potential and increasing PAH bioaccessibility and chemical activity. Environmental chemists depend on partitioning coefficients between SOM and octanol/water partitioning coefficient (K_{OW}) to determine partitioning of chemical compounds to soils and sediments [66,67]. B[a]P has high K_{OW} and greater affinity to partition into SOM but yet less biodegradable [38,67]. In such degraded soils, the total fraction of B[a]P concentration available for uptake would need to be measured to determine the risk of exposure to biota and humans using appropriate predictive procedures.

3.0 Risk assessment of PAHs in soil

3.1 Bioaccessibility and Chemical Activity

As previously noted, remediation intervention based on total concentration of TPH (5,000 mg kg^{-1}) or PAH (40 mg kg^{-1}) overestimates the risk of exposure to receptors, without considering constituent bioavailability, bioaccessibility thermodynamics or transport (pathway) to specific receptors [68,69]. Semple et al. [70] described bioavailability ‘referred to as A in Figure 3’ as that fraction of a chemical that is freely available to cross an organism’s membrane from the medium which the organism inhabits at a given time. Bioaccessibility ‘referred to as B in Figure 3’ encompasses both the bioavailable fraction and the potentially bioavailable fractions [70] (Figure 3). In regards to uptake from soil, bioavailability describes the rate of uptake or biodegradation and bioaccessibility describes the extent to which PAHs may be degraded or taken up [34]. There are however, distinguishing characteristics related to bioavailability and bioaccessibility of one PAH to another owing to differing chemical properties which affects their environmental fate [39,67]. The predictable bioaccessible fraction also refers to that which can be rapidly desorbed from the soil components (SOM or clay) and freely dissolved in pore water over time but this fractional quantity is governed by soil properties and often reduces over time due to increase in contact time [41,71]. It is the bioavailable fraction or a sub-fraction of the bioaccessible fraction (Figure 3) that can either be degraded or cause toxicity to biota. Hence in order to avoid underestimating the potential toxic fraction, using the predicted bioaccessible fraction in contaminated land risk assessment, will provide more useful information to contaminated land practitioners and can be a driving tool for guidelines on remediation. Several methods have been adopted to successfully measure the bioaccessible fraction of PAHs in soil (Table 2).

Another limitation of measuring the total quantity of dissolved and desorbable fraction is that it does not provide detailed information on the diffusion and partitioning potential of PAHs, as such, giving limited information on chemical activity of the compounds in question. The chemical activity of a compound provides information on the fate and energetic state of the chemical which quantifies the potential for diffusion to pore water and partitioning into soil particulates (SOM, clay) [73]. It thus provides valuable estimates of the measured environmental concentrations or exposure levels to potentially toxic levels [74]. Equilibrium employed to measure free dissolved concentrations are utilised to measure chemical activity of PAHs, where the equilibrium partitioning concentration in the device is multiplied by an activity coefficient [73,75]. This is then translated to chemical activity. Similar to bioaccessibility, chemical activity decreases with increasing contact-time and sorption processes and it is a dimensionless measurement between zero and one and can be derived from fugacity [73,76]. The latter (one) represents a point of pure liquid saturation of a compound which cannot be attained by either a gas or solid substance [73]. For instance, even where the concentration of a HMW PAH is low in water due to low solubility, they can possess high activities and fugacities with substantial adverse effects [67].

Normally, clay content of soil increases and SOM decreases with increasing soil depth [52]. Where the topsoil which constitutes the higher fraction of SOM becomes degraded, it reduces the capacity of soils in such regions to adsorb PAHs and diminishes agricultural productivity and stabilisation. Rather, there would be reversible partitioning of the contaminants to the mineral surfaces, hence resulting in insignificant retention of the contaminants. Further consideration is required for risk assessment, if total PAH concentration is below intervention value and there is substantial fraction of B[a]P and cohorts in the soil, risk of exposure to the confirmed carcinogen should be quantified.

3.2 Toxicity Equivalence

The US EPA recommended using toxicity equivalent factors (TEF) to assess human health risks from exposure to dioxin-like compounds in Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and Resource Conservation and Recovery Act (RCRA) contaminated sites [87]. Previously, the World Health Organisation (WHO) recommended the use of TEFs to characterise mixtures of dioxins/furans and PCBs [88]. Apparently, this was due to the prevalence and carcinogenic potential of their congeners when exposed to biota, which is highly applicable to PAH congeners as well. TEFs express the toxicity of complex mixtures potent chemical compounds to be expressed as a unitless number representing the concentration of most toxic congeners. The application of TEFs to PAHs as routinely used for dioxins and PCBs, reflect the actual risks posed by PAH contaminated sites is of special interest [89]. More recently, the TEF methodology has been used to evaluate toxicity and assess the associated risks of environmental mixtures of carcinogenic-polycyclic aromatic hydrocarbons (c-PAHs) by the department of Ecology, Washington US, United Kingdom, Australia, Provinces of Canada and the Netherlands. The mixtures of c-PAHs (benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene, benzo[b]fluorantheneare, benzo[k]fluoranthene, benzo[a]anthracene, benzo[g,h,i]perylene) are considered as a single hazardous substance when determining compliance to target levels. The European Food Safety Authority Panel on Contaminants in the Food Chain (CONTAM Panel) concluded that where either four or eight PAHs (PAH4, PAH8), individually or in combination in food, are possible indicators of the carcinogenic potency [90]. Toxicity of a complex mixture of PAHs can be addressed in order to evaluate human health risks from oral exposure to PAHs in soils. In relation to the Australian National Environment Protection Measures (NEPM) (Assessment of Site Contamination), each constituent compounds contribute has a specific toxic equivalence factor (TEF) that weights (varying from 1 to 0.01) (Table 3) its toxicity relative to that of Benzo(a)pyrene. It is assumed that the toxicity and the mode of action for all the c-PAHs are common and any toxicological interactions (antagonism, synergism) would be absent among the c-PAHs.

The TEF approach is implemented when determining compliance with remediation levels that have been previously established for mixtures of cPAHs. However, some limitations of the approach include;

- limited data from studies on potency and carcinogenicity of individual PAHs other than B[a]P,
- individual PAHs exert similar toxicological effect,
- lack of toxicological data base
- few other PAHs in mixture contribute to the incidence of carcinogenicity,
- B[a]P equivalency factors most frequently underestimate carcinogenicity and do not describe the potency of PAH mixtures. [90,91].

Notwithstanding, it remains the best of several carefully evaluated approaches where PAH4 or PAH8 is applied to manage the cancer risks of PAH-containing mixtures. In order to develop PAH remediation target values for soil and groundwater, the physic-chemical properties of individual carcinogenic c-PAHs should be used along with the soil properties. The USEPA, NEPM, WHO and CCME have already assigned individual single unitless TEF values for PAH8 (mixture of carcinogenic PAHs). This is expressed as an example in Table 3 to attain the toxic equivalent quotient (TEQ) which can be calculated by multiplying the concentration of c-PAHs in an environmental mixture by its corresponding TEF value. The value attained is compared to desired level of acceptable risk in soil quality guidelines protective of different components of the environment at immediate risk of exposure (portable water, biota, soil). This is equally done for non-carcinogenic PAHs, but where

PAHs display risk for both carcinogenic and non-carcinogenic effects, protection to cancer risk is considered for remediation [92]. Considering the c-PAH TEQ values (2.67, 4.16, 1.57 mg kg^{-1}) deduced from PAH values derived from Nduka et al. [14] and based on the TEF units provided by NEPM guidelines (Table 3), when compared to the target value (1 mg kg^{-1}) developed by EGASPIN, the value exceeds the safe limits and thus requires constructive remedial actions due to threat posed to human health. These values were compared to EGASPIN target value only as an illustration of the applicability and consideration of TEF values for human health protection. These TEQ results deduced in this paper are in accordance with literature where PAHs induce dioxin-like activity in contaminated sediments [91,93].

4.0 Mitigation of Risks Associated to PAH-Contaminated Soils

The implementation of bioremediation in remediating PAH contaminated soils has oftentimes been unsuccessful due to high toxicity, unfavourable soil properties, PAH recalcitrance, environmental conditions (e.g. consistent rainfall), nutrient inadequacy and low population of PAH-degrading organisms [57,94,95]. Following the removal of the very rapidly desorbable PAH fraction, the remaining fraction consists of a sorbed fraction that can potentially be extracted and a potentially irreversibly bound fraction within soil (Figure 3) [34,35,40,41]. The retained contaminant is thought to be sorbed through covalent bonding, partitioning or entrapment within soil organic matter, thereby rendering the contaminant immobile [40,96]. The retention of the contaminant becomes enhanced following increase in soil-PAH contact time (aging) [40,41,71] (Figure 2). Aging and the presence of carbonaceous organic matter have often been shown to be a constraint to bioremediation by reducing the bioaccessibility of PAHs in soils [40,74,97]. Recently, this constraint has been tailored to become a strength in order to control mobility and reduce the bioaccessible fraction of PAHs in soils by amending soils with biochar or activated carbon [40,41,98,99]. It is believed that c-PAHs i.e. HMW PAHs with higher K_{OW} values and sorptive capacity will be far more retained within the SOM than other PAHs, however, this may only be a risk postponed when SOM is degraded or disturbed.

Hence, using more recalcitrant ubiquitous organic matter to adsorb and contain contaminants by locking them up through chemical and physical mechanisms of binding will eventually ensure limited risk in soils. The choice of adsorbent material is a question of cost, soil properties, contaminant concentration and specific purpose. Biochar is an inexpensive and recalcitrant black carbon material derived from the pyrolysis of organic matter under specific temperature and duration regimes with wide range of applicability. Although, biochar may have contrasting features and properties, owing to nature of feedstock and production condition, it has been reported to be useful in mitigating risk of chemical exposure and remediation of contaminated soils [72,100]. Biochar has the capacity to encourage degradation of some petroleum hydrocarbons [101] and retain the more hydrophobic HMW PAHs within the network of macro-pore structure [41,102]. With regards to the latter, the contaminants desorb from soil components and are attracted to the high binding sites of biochar, where retention will depend on the volume and distribution of the macro-pores [41,98,99,103]. However, Webber et al. [104] has shown that majority of biochars exhibit more macroporous structures and that hydrophobic labile components display pore blocking effect which can limit sorptive capacity. Hence, increasing heat treatment temperature (HTT) results in dehydroxylation, inducing pore development and higher surface areas by driving off the labile phase and exposing the blocked pores [104-107]. Hence, rather than increasing biochar concentration, more emphasis will be made on increasing sorptive capacity through activation. Constructive activated biochar or activated carbon amendment/capping in degraded soils or sediments increases SOM content and also increases the sorptive capacity of the soils control mobility/transport, leaching and corresponding risk of PAH exposure. Although more research work is required, successful studies and implementations have shown by Ghosh et al. [108], Kupryianchyk et al. [109], in Superfund sites [110] and in one of the biggest remediation works in the US (Onondaga lake New York clean up exercise).

Conclusion

Over the years, assessment and remediation of contaminated land has been based on total extractable concentrations of TPH and PAHs in soil which does not consider risk of exposure to specific carcinogenic petroleum contaminants to humans and biota. There have been reported cases of catastrophic events at oil exploration facilities in Nigeria which often alters the composition of petroleum hydrocarbons and potentially increasing fractions of carcinogenic PAHs in soils constantly being degraded by erosion. There is also variation in site characteristics and fate of contaminants in soil, hence proper planning and implementation of risk assessment is required for decision making. This report proposes the implementation of risk assessment tools (bioaccessibility, chemical activity, TEQ) to be adopted for safe site investigation and management of contaminants in soil for the protection of human health and the ecosystem. In addition, the implementation of in-situ retention of contaminants that can be controlled using engineered activated biochar or activated carbon materials should be considered for adoption into risk-based approach in remediating contaminated land.

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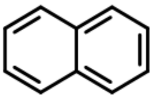
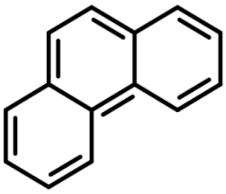
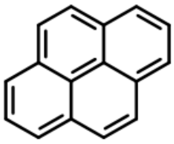


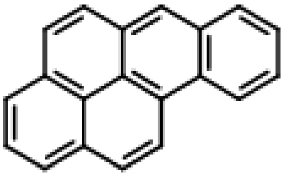
Naphthalene



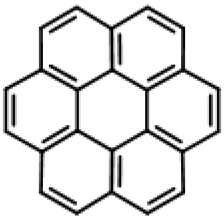
Phenanthrene



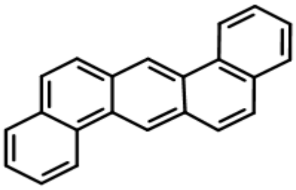
Pyrene



Benzo (a) pyrene



Coronene



Dibenz (ah) anthracene

Figure 1 Chemical structure of some polycyclic aromatic hydrocarbons (PAHs) (ChemSpider)

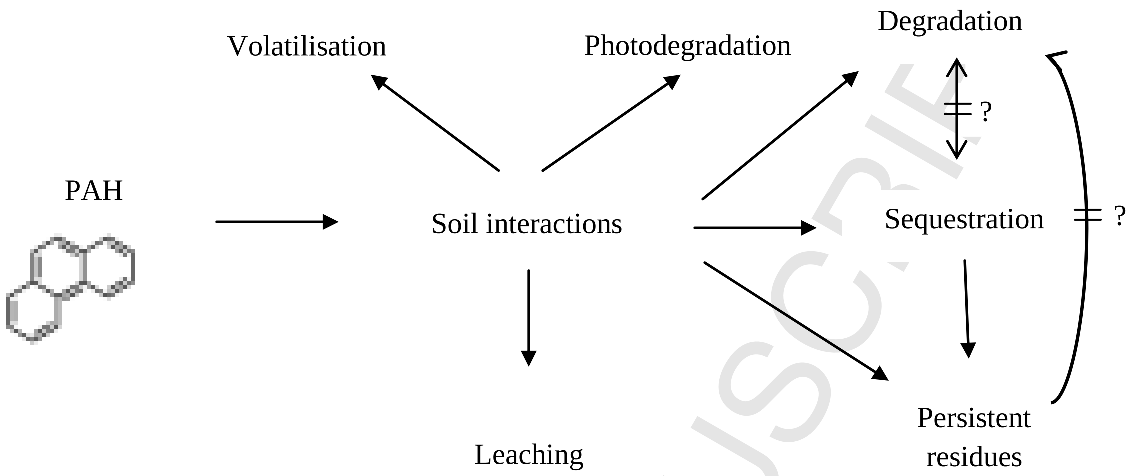


Figure 2 Fate of PAHs in soil (Adopted from Stokes et al. [36])

Table 1 Insight on surface soil texture in Southern Nigeria

Location	Clay (%)	Sand (%)	Silt (%)	CEC	OM (%)	Texture	pH	Reference
Oyo	19	36	45	14.11	5.9	L	6.5	Ogban & Babalola, [50]
	30	35	35	11.56	3.9	L	7.7	[50]
	22	41	37	11.56	8.6	L	7.4	[50]
	16	48	36	18.77	5.1	L	7.4	[50]
	31	22	47	13.31	6.2	SiL	6.1	[50]
	28	47	25	18.89	4.2	SiL	6.2	[50]
Kogi	13	85	2	123.6	2.8	SL	7.1	Amhakhian & Achimugu, [51]
	19	79	2	79.46	0.9	LS	5.8	[51]
	10	88	2	NA	0.4	S	5.7	[51]
Ekiti	15.4	69.2	15.4	1.27	2.6	SL	6.1	Fasina et al. [52]
	25.4	61.2	13.4	1.20	0.4	SL	5.8	[52]
	13.4	71.2	15.4	1.13	2.5	SL	5.5	[52]
Ogun	18.0	66.0	16.0	5.5	15.8	SL	4.5	Fasina et al. [49]
	6.0	90.0	4.0	4.7	15.5	S	4.8	[49]
	6.0	90.0	4.0	6.1	11.0	S	4.3	[49]
	4.0	88.0	8.0	6.8	7.2	LS	5.3	[49]
Imo	12.3	85.7	2.0	3.68	1.8	LS	6.7	Ujowundu et al. [53]
	15.3	81.7	3.0	2.10	4.0	LS	5.9	[53]
Delta	20.8	67.8	12.2	1.87	70.0		5.9	Okoro [54]
	17.4	68.2	14.5	1.35	6.1		6.2	[54]
Rivers	1.2	92.6	6.2	3.3	0.9		5.9	Nwankwo et al. [55]
	1.0	95.4	2.6	8.7	0.4		5.1	[55]
	0.4	94.3	5.3	8.7	3.3		5.1	[55]

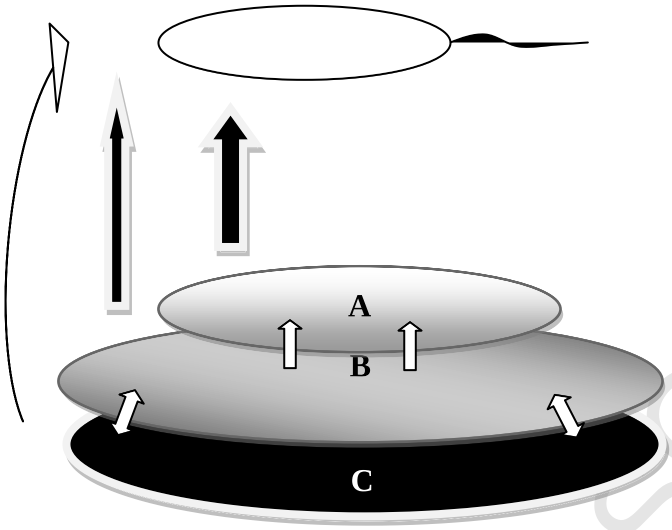


Figure 3 Bioaccessibility of PAHs in soil where A, B and C represent the bioavailable, bioaccessible and non-bioaccessible fractions, respectively (Adopted from Ogbonnaya and Semple, [72])

Table 2 Measurements of bioaccessibility and chemical activity

Measurement	Technique	Reference
Bioaccessibility	Respirometric assay	Reid et al. [77]; Stokes et al. [36]
	Cyclodextrin extraction	Rhodes et al. [71]; Sanchez-Trujillo et al. [32]; Ogbonnaya et al. [41]
	Gastro-intestinal extraction	Lu et al. [78]
	butanol extraction	Yang et al., [79]
	Tenax extraction	Yang et al., [79]
Chemical activity	Polydimethylsiloxane vial coating	Reichenberg et al. [80]
	SPME fibre	Mayer et al. [81]; Marchal et al. [82]
	Low-density polyethylene strips	Booij et al. [83]
	Liquid filled hollow fibre	Liu et al. [84]
	Polyoxymethylene plates	Jonker and Koelman, [85]
	Thin-film solid phase extraction	Wilcockson and Gobas, [86]

Table 3 Application of TEF values to contaminated site

c-PAHs	Site A	Site B	Site C	TEF	TEQ(A)	TEQ(B)	TEQ(C)
Benz[a]anthracene	0.53	1.04	0.07	0.1	0.53	1.04	0.07
Chrysene	0.12	0.22	0.01	0.01	0.00	0.00	0.00
Benzo[b]fluoranthene	0.06	0.11	0.01	0.1	0.01	0.01	0.00
Benzo[k]fluoranthene	0.31	0.66	0.12	0.1	0.03	0.07	0.01
Benzo[a]pyrene	1.71	2.40	1.16	1	1.71	2.40	1.16
Benzo[ghi]perylene	0.01	0.00	0.00	0.01	0.00	0.00	0.00
Dibenzo[ah]anthracene	0.36	0.60	0.13	1	0.36	0.60	0.30
Indeno[123-cd]pyrene	0.34	0.38	0.29	0.1	0.03	0.04	0.03
Total TEQ					**2.67**	**4.16**	**1.57**

TEQ refers to toxicity equivalent quotient
Site A,B,C are concentrations of PAHs from literature in mg kg^{-1} [93] (Nduka et al., 2013)
TEQ (A,B,C) refers to TEQ of individual sites