Accepted Manuscript

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

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Please cite this article as: Ogbonnaya, U.O., Oyelami, A.O., Umego, M.O., Okere, U.V., David, O.A., Fasina, S.A., Semple, K.T., Assessment of PAH contaminated land: Implementing a risk-based approach. *Environmental Technology & Innovation* (2017), http://dx.doi.org/10.1016/j.eti.2017.06.001

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
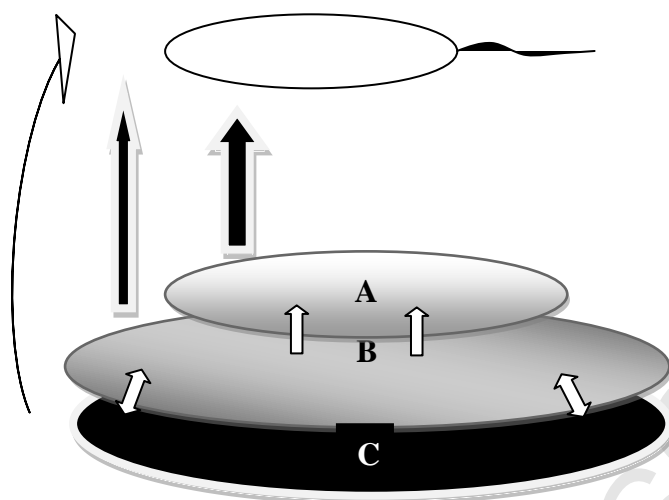
- Specific biochar can be used to mitigate risks

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])

1   **Assessment of PAH contaminated land: Implementing a risk-based**

2   **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.

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.

75 EGASPIN recommends the use of the Risk-Based Corrective Action (RBCA) often referred

76 to as "Rebecca" approach for contaminated land remediation, considering an intervention

77 value of 5,000 mg kg^{-1} for mineral oil which is oftentimes referred to as total petroleum

78 hydrocarbons (TPH). Historically, TPH has usually been the main criterion for environmental

79 management of oil and gas operational locations internationally, owing to the development of

80 acceptable health risk-based TPH levels [3]. Chemicals of critical concern such as polycyclic

81 aromatic hydrocarbons (PAHs) and heavy metals found in crude oil and their derivatives are

82 often in low concentrations, potentially posing a low risk to receptors [3-5]. This does not

83 rule out that the ambiguous TPH measurement alone can either be under or over protective to

84 receptors, since petroleum chemical composition and properties can vary from site to site. In

85 addition, TPH measurement does not take into account the land-use where oil and gas facility

86 is located, method of spill (vandalisation of pipelines or explosion), illegal refining (still on-

87 going), blow out of abandoned oil wells and the destruction of petroleum products found by

88 security operatives in Nigeria. These activities often alter the nature and composition of crude

89 oil and its derivatives, which can significantly increase the level of specific concerned

90 contaminants.

91

92 The constituents of TPH include::alkanes, alkylated alkenes, cyclic alkanes, phenols,

93 organosulphur and organonitrogen compounds, acids, alkynes, alkyl benzenes and PAHs [5].

94 The consequences of releasing such compounds are far reaching since petroleum

95 hydrocarbons together with heavy metals (lead, iron, cadmium, nickel) are released into the

96 environment, thus contaminating the air, surface and ground waters, sediments, soils,

97 vegetation and organisms. In some instances, there have been reported cases of fire outbreak

98 due to such activities, hence, the regulatory system and policy for contaminated land

99 remediation requires a more systematic approach considering chemical indicators and

100 fractions in risk assessments. Hence, DPR initiated the intervention and target values for

101 petroleum contaminants as protective and remedial endpoints for site assessment and

102 remediation. The intervention value indicates quality for which the functionality of soil for

103 human, animal and plant life are being threatened or seriously impaired with concentrations $\geq$

104 5,000 mg kg^{-1} and $\geq$ 40 mg kg^{-1} for TPH (mineral oil) and PAHs, respectively [6]. The target

105 value indicates soil quality required for sustainability in terms of remedial policy, the soil

106 quality required for full restoration of soil's functionality for human, animal and plant life

107 which is 50 mg kg^{-1} and 1 mg kg^{-1} for TPH (mineral oil) and PAH, respectively. Thus, this is

108 the soil quality aimed for as requested by DPR [6]. A major weakness of the Nigerian

109 standard is that where there is relative high risk of contaminant exposure and presence of

110 carcinogenic PAHs at concentrations below the intervention values, no action is required to

111 be taken. In contrast, the Dutch Environmental Standards considers levels below the

112 intervention value where there is obvious human exposure. In addition, more emphasis is

113 paid to TPH remediation without considering the risk posed by specific persistent and toxic

114 contaminants present in the TPH continuum or generated during land-use.

115

116 PAHs are a class of organic contaminants dispersed into the environment through incomplete

117 combustion of organic materials and by natural processes [7,8]. PAHs are composed of two

118 or more fused aromatic rings in linear or clustered arrangements containing carbon and

119 hydrogen atoms with nitrogen, sulphur, and oxygen atoms substituted with the benzene ring

120 to form heterocyclic aromatic compounds [9]. They are dominantly lipophilic in nature and

121 have been classified into two subgroups which are the low molecular weights (LMW) (two or

122 three fused rings) and high molecular weights (HMW) (four or more fused rings) (Figure 1).

123 Majority of PAHs are considered to be low in concentrations but pose more toxic and

124 recalcitrance under normal conditions, hence, total TPH concentration as a tool for risk-based

125 approach to remediate all hydrocarbon polluted site therefore has limited benefits. This paper

126 promotes the implementation of specific chemical risk-based assessment of petroleum

127 contaminated sites based on land properties, land-use and method of spill. It also considers

128 the differences in soil within Nigeria, which affects the fate and transport of PAHs in the soil

129 environment.

130

131 **2.0   Production of polycyclic aromatic hydrocarbons**

132 PAHs have been of growing concern due to consistent release, persistence, toxicity and

133 transport. Most of the inputs are anthropogenic and thus can be controlled by avoidance,

134 minimisation, recovery or treatment. The major sources of anthropogenic inputs into the

135 environment are: automobile fuel combustion, pyrolytic processes, waste incinerators,

136 domestic heaters, spillage of petroleum products, creosote wood treatment facilities, gas

137 stations, sewage discharge and waste dumping, cigarette smoking, barbeque and roasting

138 food, shipping and boating activities [10-14]. Thus, PAHs are ubiquitous as they can be

139 found in soils, sediment, water and air particulates, with a potential of human exposure

140 through the atmosphere, food and soil contact [15-17]. They are highly recalcitrant

141 molecules, especially when they are HMWs and can cause carcinogenic, mutagenic, kidney

142 and liver damages in humans [18]. Their formation can vary with substrate, fuel type and

143 actual pyrolysis conditions [19-21].

144

145 In detail, during combustion of light hydrocarbons such as acetylene and methane, several

146 radicals are produced in the gas phase, and the combination of propargyl radicals (C_3H_3) lead

147 to the formation of benzene [19,22,23]. Propargyl and acetylene (C_2H_2) can also react to

148 produce cyclopentadienyl radicals (C_5H_5) [21] or two step hydrogen abstraction and

149 acetylene addition (HACA) mechanism on benzene produces naphthalene [19,21].

150 Alternatively, the cyclopentadienyl radical can undergo radical recombination to form

151 naphthalene with loss of hydrogen [24-26]. Following benzene pyrolysis, aromatic growth is

152 initiated to form biphenyl, which in the presence of acetylene forms phenanthrene [21].

153 Subsequently, HACA mechanism on lower molecular weight (LMW) PAHs, such as

154 naphthalene and phenanthrene occurs where hydrogen abstraction creates a surface radical,

155 acetylene addition to the radical formed and followed by ring cyclisation leads to the

156 formation of higher molecular weight (HMW) PAHs [21,25,27]. Alternatively, reaction of

157 the phenyl ring with a PAH accompanied by acetylene addition and dehydrocyclisation

158 produces a five-membered ring PAH [28]. Increasing time and temperature of combustion

159 leads to increasing yields of all PAHs, especially the three-, four- and five-ring PAHs,

160 accompanied by the formation of numerous methyl and phenyl substituted PAHs [20]. This is

161 an obvious situation that occurs within the Niger Delta region of Nigeria where illegal

162 refining activity occurs (artisanal refining), destruction of petroleum products, blow out of

163 production wells or any condition where combustion of fossil fuel occurs. When these

164 compounds are dispersed into the environment, they are mainly deposited through wet or dry

165 deposition onto soil via point or diffuse sources [13,29]. The concentrations of PAHs within

166 the soil vary, due to proximity to source, environmental conditions and properties of media in

167 which it is found [16,30]. LMW PAHs can also exist in more complex mixtures as creosote,

168 soot and coal tars [20,21,31], When LMW PAHs are more dominant (60-70%), it is

169 suggested that the source of PAHs is fresh liquid spill, whereas when HMW PAHs are more

170 abundant, it is suggested that the source is of pyrogenic origin [11,32].

171

172 **2.1   Behaviour of PAHs in the soil environment**

173 Detailed information is available in literature on the fate of PAHs in soil [33,34]. Briefly,

174 when PAHs gain access to soil, fractions may be lost through volatilisation, leaching, or

175 degradation at varying rates and extents due to differences in PAH physic-chemical

176 properties and soil characteristics [35-39]. These processes (volatilisation, leaching and

177 degradation) remove the mobile fractions, bioavailable and rapidly desorbable fractions of

178 PAHs from soils leaving residual fractions that subsequently persist for a longer period of

179 time [36,40,41] (Figure 2). However, microbial degradation of organic contaminants, such as

180 PAHs stand out as the major mechanism for their removal, hence this process has often been

181 favoured, stimulated and implemented in remediation of contaminated land globally.

182

183 The biodegradation of a PAH is hence limited to intrinsic properties, soil properties,

184 indigenous microbial population, chemical toxicity and environmental conditions. Hence, a

185 highly toxic and recalcitrant PAH like benzo (a) pyrene (B[a]P) can readily be sorbed into the

186 soil matrix (SOM, clay) thereby reducing its bioaccessible fraction to microorganisms [38].

187 The residual or non-bioaccessible fractions of PAHs also implies it is poorly available to

188 organisms and could hence be considered as being inert and pose less risk following proper

189 management. However, if the soil texture does not favour sorption of such contaminant,

190 fractions of the parent compound and the metabolites pose considerable risk to receptors

191 [42,43].

192

193 **2.2   Soil Texture and Conditions**

194 The soil texture varies greatly in different areas of Southern Nigeria where majority of oil

195 exploration activities occur (Table 1). In addition to the inherent physical properties of the

196 soils, the soils within southern Nigeria are in areas of high rainfall exceeding 2,000 mm with

197 high intensities, high erositivity and undulating topography [44-46]. Land or soil degradation

198 associated with wind and water erosion in Sub Sahara Africa has been extensively reported

199 [47-49]. Although Table 1 does not give a total overview and variation of all the soils in

8

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

225 oil spills were reported to be due to artisanal activities, sabotage by bursting of delivery pipes

226 and theft of unrefined or refined oil at various quantities. Spills of smaller amounts have been

227 due to aged pipes, equipment failure, natural incident, accident and maintenance error [2,59].

228 The composition of the spills however differs due to source, process of spill event and

229 remediation process. For instance Ezenne et al. [60] showed that composition of TPH and

230 PAH can differ in concentration despite having same source owing to different processing in

231 soils. Most site assessment studies in Nigeria have focused on TPH concentration, without

232 considering PAH fractions which constitute more toxic and persistent contaminants. For

233 instance, following oil spills over 15 years ago in a community where oil and gas exploration

234 activities took place in Rivers State, Nigeria, soil samples were collected at various depths

235 and homogenised [61]. At the two most contaminated sites, mean TPH concentration ranged

236 from 101 mg kg^{-1} to 1,651 mg kg^{-1}, with groundwater concentration exceeding 12,000 mg kg^{-1}

237 ^{1}. Although the authors did not provide information on the mode of spillage, it shows that

238 groundwater can be contaminated by leaching, depending on the properties of soil and

239 persistence of spillage. Okop and Ekpo [62] also showed that soil samples around a well head

240 of an oil pipeline contained TPH levels between 54 mg kg^{-1} and 345 mg kg^{-1}. This was due to

241 spillage of crude oil from the aged facility.

242

243 Similarly, soil samples were collected around a depot facility carrying refined petroleum

244 products in Aba, Abia state Nigeria at three different depths (0-10, 10-20, 20-30 cm). The

245 concentrations of TPH ranged from 5,120 mg kg^{-1} (20-30 cm depth) to 24,900 mg kg^{-1} (0-10

246 cm depth) [63], whilst a control site had less than 1 m kg^{-1} TPH concentration. The author

247 observed that total PAH concentration did not exceed 1% of the value of TPH concentration

248 at each depth but it exceeded the PAH concentration at control site. This showed that the spill

249 of oil within the site may be due to corrosive pipes or tanks and the low PAH fraction would

10

250   have been part of the TPH in the refined product. Similarly, soil samples collected from

251   diesel storage sites located in Imo state recorded 46,726 mg kg^{-1} and 844 mg kg^{-1} of TPH and

252   PAH, respectively, showing the presence of PAH in diesel oil [53]. Although below 2% of

253   TPH, the high PAH concentration was due to aging of the contaminant within the soil around

254   the storage site. More recently, Okpashi et al. [64] determined the TPH and total PAH

255   concentration in soils following crude oil overflow by a flow-station owned by an oil

256   company located in Delta state, Nigeria. The authors found 15,056 mg kg^{-1} and 2,462 mg kg^{-1}

257   of TPH and PAHs, respectively present in the soils.

258

259   Over thirty years ago, an undisclosed quantity of crude oil spilled from an unknown source

260   around Ejamah Ebubu in Eleme Local Government area of Rivers State, where a pipeline

261   running inside the town existed [65]. The spill flowed along the topographic slope,

262   contaminating the soils and surface waters and the crude oil ignited and burned for several

263   days before the fire was brought under control. The concentrations of TPH and the associated

264   benzene, toluene, ethylene and xylene (BTEX) and PAH fractions within the swamp

265   sediment were investigated. Results showed that TPH ranged from 14.6 mg kg^{-1} to 28,687 mg

266   kg^{-1} with an average value of 4,979 mg kg^{-1}, BTEX values did not exceed 0.1 mg kg^{-1} and

267   PAH values ranged from 8.42 mg kg^{-1} to 14,130 mg kg^{-1} with an average value of 2,517 mg

268   kg^{-1} [65]. In another study by Mmom and Deekor [57], well-drained and water-logged acidic

269   soils within the mangrove area inhabiting oil exploration activities, had varying

270   concentrations of TPH and PAH with minimal BTEX. TPH concentrations ranged between

271   3,100 mg kg^{-1} and 6,600 mg kg^{-1}, whilst PAH fractions ranged between 2,100 mg kg^{-1} and

272   4,100 mg kg^{-1}. Interestingly, PAH fractions ranged from 46% to 86% of the value of TPH

273   which indicates a remarkable proportion suggesting most of the sites had experienced ignition

274   thereby raising PAH concentrations. The authors implemented a land farming

275   (bioremediation) approach to degrade the petroleum contaminants but this failed to ensure the

276   concentrations of PAHs go below 1,268 mg kg^{-1}. In fact, a maximum of approximately 50%

277   of total PAHs was biodegraded, owing to the acidic nature, water logging of soil and toxicity

278   of the PAHs.

279

280   Based on the above studies, although TPH may be reduced to values permissible by the

281   regulatory bodies through biodegradation, contaminated soils can still exhibit highly toxic

282   characteristics due to the PAH concentrations within. Stroud et al. [38] demonstrated rapid

283   removal of aliphatic hydrocarbon followed by the PAHs, with the HMW PAHs (pyrene,

284   B[a]P) being more persistent having low catabolic potential. The concentration of inherent

285   PAHs in petroleum products may be sufficiently low, but when hazardous events associated

286   with elevated temperatures occur (explosions, fire outbreak, ignition or bush burning),

287   increases in PAH concentration occurs, hence increasing the toxic conditions. As previously

288   indicated in this current paper, most of the soils within southern Nigeria region exhibit low

289   OM content and clay (vulnerable and degraded soils), reducing PAH sorptive potential and

290   increasing PAH bioaccessibility and chemical activity. Environmental chemists depend on

291   partitioning coefficients between SOM and octanol/water partitioning coefficient (K_{OW}) to

292   determine partitioning of chemical compounds to soils and sediments [66,67]. B[a]P has high

293   K_{OW} and greater affinity to partition into SOM but yet less biodegradable [38,67]. In such

294   degraded soils, the total fraction of B[a]P concentration available for uptake would need to be

295   measured to determine the risk of exposure to biota and humans using appropriate predictive

296   procedures.

297

298   **3.0   Risk assessment of PAHs in soil**

299   **3.1   Bioaccessibility and Chemical Activity**

300 As previously noted, remediation intervention based on total concentration of TPH (5,000 mg

301 kg^{-1}) or PAH (40 mg kg^{-1}) overestimates the risk of exposure to receptors, without

302 considering constituent bioavailability, bioaccessibility thermodynamics or transport

303 (pathway) to specific receptors [68,69]. Semple et al. [70] described bioavailability 'referred

304 to as A in Figure 3' as that fraction of a chemical that is freely available to cross an

305 organism's membrane from the medium which the organism inhabits at a given time.

306 Bioaccessibility 'referred to as B in Figure 3' encompasses both the bioavailable fraction and

307 the potentially bioavailable fractions [70] (Figure 3). In regards to uptake from soil,

308 bioavailability describes the rate of uptake or biodegradation and bioaccessibility describes

309 the extent to which PAHs may be degraded or taken up [34]. There are however,

310 distinguishing characteristics related to bioavailability and bioaccessibility of one PAH to

311 another owing to differing chemical properties which affects their environmental fate [39,67].

312 The predictable bioaccessible fraction also refers to that which can be rapidly desorbed from

313 the soil components (SOM or clay) and freely dissolved in pore water over time but this

314 fractional quantity is governed by soil properties and often reduces over time due to increase

315 in contact time [41,71]. It is the bioavailable fraction or a sub-fraction of the bioaccessible

316 fraction (Figure 3) that can either be degraded or cause toxicity to biota. Hence in order to

317 avoid underestimating the potential toxic fraction, using the predicted bioaccessible fraction

318 in contaminated land risk assessment, will provide more useful information to contaminated

319 land practitioners and can be a driving tool for guidelines on remediation. Several methods

320 have been adopted to successfully measure the bioaccessible fraction of PAHs in soil (Table

321 2).

322

323 Another limitation of measuring the total quantity of dissolved and desorbable fraction is that

324 it does not provide detailed information on the diffusion and partitioning potential of PAHs,

325 as such, giving limited information on chemical activity of the compounds in question. The

326 chemical activity of a compound provides information on the fate and energetic state of the

327 chemical which quantifies the potential for diffusion to pore water and partitioning into soil

328 particulates (SOM, clay) [73]. It thus provides valuable estimates of the measured

329 environmental concentrations or exposure levels to potentially toxic levels [74]. Equilibrium

330 employed to measure free dissolved concentrations are utilised to measure chemical activity

331 of PAHs, where the equilibrium partitioning concentration in the device is multiplied by an

332 activity coefficient [73,75]. This is then translated to chemical activity. Similar to

333 bioaccessibility, chemical activity decreases with increasing contact-time and sorption

334 processes and it is a dimensionless measurement between zero and one and can be derived

335 from fugacity [73,76]. The latter (one) represents a point of pure liquid saturation of a

336 compound which cannot be attained by either a gas or solid substance [73]. For instance,

337 even where the concentration of a HMW PAH is low in water due to low solubility, they can

338 possess high activities and fugacities with substantial adverse effects [67].

339

340 Normally, clay content of soil increases and SOM decreases with increasing soil depth [52].

341 Where the topsoil which constitutes the higher fraction of SOM becomes degraded, it reduces

342 the capacity of soils in such regions to adsorb PAHs and diminishes agricultural productivity

343 and stabilisation. Rather, there would be reversible partitioning of the contaminants to the

344 mineral surfaces, hence resulting in insignificant retention of the contaminants. Further

345 consideration is required for risk assessment, if total PAH concentration is below intervention

346 value and there is substantial fraction of B[a]P and cohorts in the soil, risk of exposure to the

347 confirmed carcinogen should be quantified.

348

349 **3.2   Toxicity Equivalence**

350 The US EPA recommended using toxicity equivalent factors (TEF) to assess human health

351 risks from exposure to dioxin-like compounds in Comprehensive Environmental Response,

352 Compensation, and Liability Act (CERCLA) and Resource Conservation and Recovery Act

353 (RCRA) contaminated sites [87]. Previously, the World Health Organisation (WHO)

354 recommended the use of TEFs to characterise mixtures of dioxins/furans and PCBs [88].

355 Apparently, this was due to the prevalence and carcinogenic potential of their congeners

356 when exposed to biota, which is highly applicable to PAH congeners as well. TEFs express

357 the toxicity of complex mixtures potent chemical compounds to be expressed as a unitless

358 number representing the concentration of most toxic congeners. The application of TEFs to

359 PAHs as routinely used for dioxins and PCBs, reflect the actual risks posed by PAH

360 contaminated sites is of special interest [89]. More recently, the TEF methodology has been

361 used to evaluate toxicity and assess the associated risks of environmental mixtures of

362 carcinogenic-polycyclic aromatic hydrocarbons (c-PAHs) by the department of Ecology,

363 Washington US, United Kingdom, Australia, Provinces of Canada and the Netherlands. The

364 mixtures of c-PAHs (benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, indeno[1,2,3-

365 cd]pyrene, benzo[b]fluorantheneare, benzo[k]fluoranthene, benzo[a]anthracene,

366 benzo[g,h,i]perylene) are considered as a single hazardous substance when determining

367 compliance to target levels. The European Food Safety Authority Panel on Contaminants in

368 the Food Chain (CONTAM Panel) concluded that where either four or eight PAHs (PAH4,

369 PAH8), individually or in combination in food, are possible indicators of the carcinogenic

370 potency [90]. Toxicity of a complex mixture of PAHs can be addressed in order to evaluate

371 human health risks from oral exposure to PAHs in soils. In relation to the Australian National

372 Environment Protection Measures (NEPM) (Assessment of Site Contamination), each

373 constituent compounds contribute has a specific toxic equivalence factor (TEF) that weights

374 (varying from 1 to 0.01) (Table 3) its toxicity relative to that of Benzo(a)pyrene. It is assumed

375 that the toxicity and the mode of action for all the c-PAHs are common and any toxicological

376 interactions (antagonism, synergism) would be absent among the c-PAHs.

377

378 The TEF approach is implemented when determining compliance with remediation levels

379 that have been previously established for mixtures of cPAHs. However, some limitations of

380 the approach include;

381 • limited data from studies on potency and carcinogenicity of individual PAHs other

382 than B[a]P,

383 • individual PAHs exert similar toxicological effect,

384 • lack of toxicological data base

385 • few other PAHs in mixture contribute to the incidence of carcinogenicity,

386 • B[a]P equivalency factors most frequently underestimate carcinogenicity and do not

387 describe the potency of PAH mixtures. [90,91].

388

389 Notwithstanding, it remains the best of several carefully evaluated approaches where PAH4

390 or PAH8 is applied to manage the cancer risks of PAH-containing mixtures. In order to

391 develop PAH remediation target values for soil and groundwater, the physic-chemical

392 properties of individual carcinogenic c-PAHs should be used along with the soil properties.

393 The USEPA, NEPM, WHO and CCME have already assigned individual single unitless TEF

394 values for PAH8 (mixture of carcinogenic PAHs). This is expressed as an example in Table 3

395 to attain the toxic equivalent quotient (TEQ) which can be calculated by multiplying the

396 concentration of c-PAHs in an environmental mixture by its corresponding TEF value. The

397 value attained is compared to desired level of acceptable risk in soil quality guidelines

398 protective of different components of the environment at immediate risk of exposure

399 (portable water, biota, soil). This is equally done for non-carcinogenic PAHs, but where

400 PAHs display risk for both carcinogenic and non-carcinogenic effects, protection to cancer

401 risk is considered for remediation [92]. Considering the c-PAH TEQ values (2.67, 4.16, 1.57

402 mg kg^{-1}) deduced from PAH values derived from Nduka et al. [14] and based on the TEF

403 units provided by NEPM guidelines (Table 3), when compared to the target value (1 mg kg^{-1})

404 developed by EGASPIN, the value exceeds the safe limits and thus requires constructive

405 remedial actions due to threat posed to human health. These values were compared to

406 EGASPIN target value only as an illustration of the applicability and consideration of TEF

407 values for human health protection. These TEQ results deduced in this paper are in

408 accordance with literature where PAHs induce dioxin-like activity in contaminated sediments

409 [91,93].

410

411 **4.0   Mitigation of Risks Associated to PAH-Contaminated Soils**

412 The implementation of bioremediation in remediating PAH contaminated soils has oftentimes

413 been unsuccessful due to high toxicity, unfavourable soil properties, PAH recalcitrance,

414 environmental conditions (e.g. consistent rainfall), nutrient inadequacy and low population of

415 PAH-degrading organisms [57,94,95]. Following the removal of the very rapidly desorbable

416 PAH fraction, the remaining fraction consists of a sorbed fraction that can potentially be

417 extracted and a potentially irreversibly bound fraction within soil (Figure 3) [34,35,40,41].

418 The retained contaminant is thought to be sorbed through covalent bonding, partitioning or

419 entrapment within soil organic matter, thereby rendering the contaminant immobile [40,96].

420 The retention of the contaminant becomes enhanced following increase in soil-PAH contact

421 time (aging) [40,41,71] (Figure 2). Aging and the presence of carbonaceous organic matter

422 have often been shown to be a constraint to bioremediation by reducing the bioaccessibility

423 of PAHs in soils [40,74,97]. Recently, this constraint has been tailored to become a strength

424 in order to control mobility and reduce the bioaccessible fraction of PAHs in soils by

425 amending soils with biochar or activated carbon [40,41,98,99]. It is believed that c-PAHs i.e.

426 HMW PAHs with higher K_{OW} values and sorptive capacity will be far more retained within

427 the SOM than other PAHs, however, this may only be a risk postponed when SOM is

428 degraded or disturbed.

429

430 Hence, using more recalcitrant ubiquitous organic matter to adsorb and contain contaminants

431 by locking them up through chemical and physical mechanisms of binding will eventually

432 ensure limited risk in soils. The choice of adsorbent material is a question of cost, soil

433 properties, contaminant concentration and specific purpose. Biochar is an inexpensive and

434 recalcitrant black carbon material derived from the pyrolysis of organic matter under specific

435 temperature and duration regimes with wide range of applicability. Although, biochar may

436 have contrasting features and properties, owing to nature of feedstock and production

437 condition, it has been reported to be useful in mitigating risk of chemical exposure and

438 remediation of contaminated soils [72,100]. Biochar has the capacity to encourage

439 degradation of some petroleum hydrocarbons [101] and retain the more hydrophobic HMW

440 PAHs within the network of macro-pore structure [41,102]. With regards to the latter, the

441 contaminants desorb from soil components and are attracted to the high binding sites of

442 biochar, where retention will depend on the volume and distribution of the macro-pores

443 [41,98,99,103]. However, Webber et al. [104] has shown that majority of biochars exhibit

444 more macroporous structures and that hydrophobic labile components display pore blocking

445 effect which can limit sorptive capacity. Hence, increasing heat treatment temperature (HTT)

446 results in dehydroxylation, inducing pore development and higher surface areas by driving

447 off the labile phase and exposing the blocked pores [104-107]. Hence, rather than increasing

448 biochar concentration, more emphasis will be made on increasing sorptive capacity through

449 activation. Constructive activated biochar or activated carbon amendment/capping in

450 degraded soils or sediments increases SOM content and also increases the sorptive capacity

451 of the soils control mobility/transport, leaching and corresponding risk of PAH exposure.

452 Although more research work is required, successful studies and implementations have

453 shown by Ghosh et al. [108], Kupryianchyk et al. [109], in Superfund sites [110] and in one

454 of the biggest remediation works in the US (Onondaga lake New York clean up exercise).

455

Conclusion

457 Over the years, assessment and remediation of contaminated land has been based on total

458 extractable concentrations of TPH and PAHs in soil which does not consider risk of exposure

459 to specific carcinogenic petroleum contaminants to humans and biota. There have been

460 reported cases of catastrophic events at oil exploration facilities in Nigeria which often alters

461 the composition of petroleum hydrocarbons and potentially increasing fractions of

462 carcinogenic PAHs in soils constantly being degraded by erosion. There is also variation in

463 site characteristics and fate of contaminants in soil, hence proper planning and

464 implementation of risk assessment is required for decision making. This report proposes the

465 implementation of risk assessment tools (bioaccessibility, chemical activity, TEQ) to be

466 adopted for safe site investigation and management of contaminants in soil for the protection

467 of human health and the ecosystem. In addition, the implementation of in-situ retention of

468 contaminants that can be controlled using engineered activated biochar or activated carbon

469 materials should be considered for adoption into risk-based approach in remediating

470 contaminated land.

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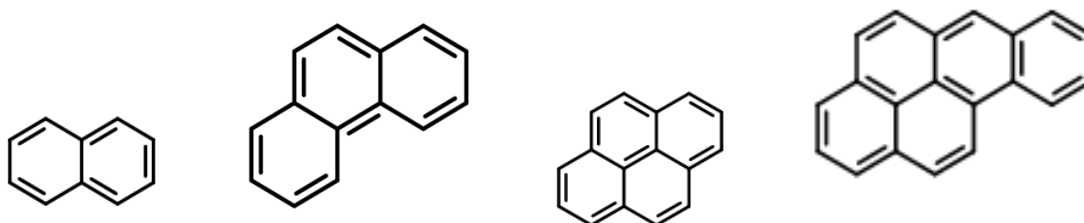
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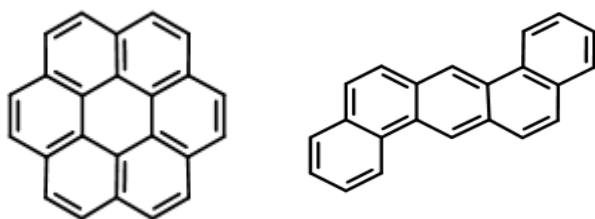806

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809   Naphthalene   Phenanthrene   Pyrene   Benzo (a) pyrene

810   Coronene   Dibenz (ah) anthracene

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

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

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870   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]

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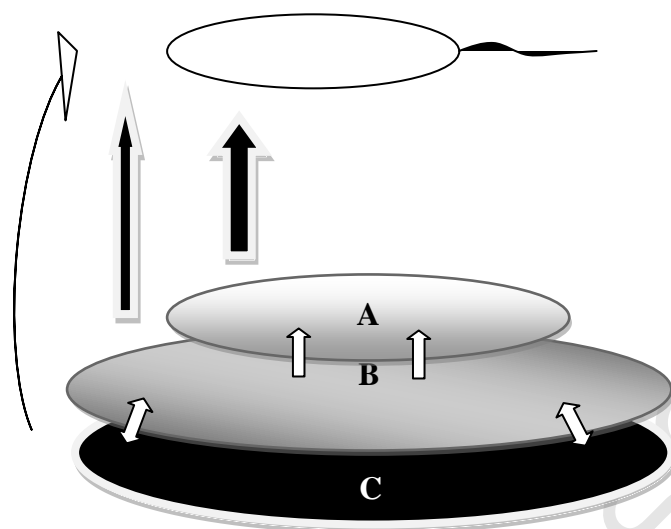
Figure 3 Bioaccessibility of PAHs in soil where A, B and C represent the bioavailable, bioaccessible and non-bioaccessible fractions, respectively (Adopted from Ogbonnaya and Semple, [72])

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913   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]

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931   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**

932   TEQ refers to toxicity equivalent quotient

933   Site A,B,C are concentrations of PAHs from literature in mg kg^{-1} [93] (Nduka et al., 2013)

934   TEQ (A,B,C) refers to TEQ of individual sites

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