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RESEARCH ARTICLE

Impact of Hydrocarbon and Heavy Metal Concentrations on Remediated Sites in Bodo, Rivers State, Nigeria

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Abstract

Crude oil spills as a result of pipeline explosions, artisanal refinery, and tanker disasters, which negatively impact soil, water, and biota in the Niger Delta region. Some polluted sites in the Niger Delta have been cleaned through concerted remediation efforts. However, many sites cleaned had been re-oiled from pipeline leaks from sabotage and artisanal refineries operated across the region. To ascertain the extent of pollution in some remediated sites in Bodo a study was carried out to investigate the concentration of total petroleum hydrocarbon (TPH) and heavy metal concentration in water sediment and biota (crabs and mudskipper). The samples were collected in situ, preserved in a cooler, and sent to the laboratory for the analyses of TPH, cadmium, lead, chromium, and lead. The result reveals a significant difference in TPH and heavy metal concentration between surface water and sediment ($P<0.001$). In contrast, there is no significant difference in chemical concentration between the dry and wet seasons or across months. Regarding biota, the ANOVA result reveals a significant difference between biota ($F3, 36 = 8.21$, $P< 0.001$). A higher concentration of Cadmium and Chromium was found in swimming crabs (*Callinectes. amnicola*), and a high cadmium concentration was found in fiddler crabs (*Uca tangeri*). At the same time, mudskipper (*Periphthalmus. babarus*) had the highest manganese concentration. The Tukey HSD test shows that the fiddler crab has the most significant chemical concentration from the permissible limit. The result implies that cleaned-up sites still have high concentration of harmful chemicals which poses a risk to human health.

Keywords: Biota, Heavy Metals, Mangrove Ecosystem, Pollution, Remediation.

1. Introduction

Petroleum hydrocarbon (PHS) are composed of short-chain hydro carbons such as paraffin, alicyclic, and aromatic compounds (Magam et al. 2024). PHS are extensively used worldwide as the major energy source for industry and daily life (Kuppusamy et al. 2020) with the increasing population and modernization, petrochemical products are in heavy demand. PHs contamination occurs regularly during exploration, production, maintenance, transportation, and storage. Similarly, accidental oil spill has disastrous and catastrophic consequences on humans and other biotic components of the ecosystem (Falih et al. 2024). Petroleum hydrocarbon usually occurs in the course of exploration, manufacturing, preservation, carriage, storage, facility, accidental spill (George et al. 2024). Oil contaminated environment has devastating and destructive significance on humans and other organic components of the ecosystem (Numbere et al. 2023). The release of these harmful compounds into the environment leads to contamination and death of organisms. Heavy metals are naturally existing in the

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soil, nevertheless due to anthropogenic activities they increase beyond acceptable limit (Onyena et al. 2024). It has been observed that hydrocarbon-polluted sites contain heavy metals and are difficult to bio-remediate (Oyetibo et al. 2017; Ossai et al. 2020). The reason is that heavy metals and metalloids limit microbial action rendering it inadequate to degrade hydrocarbon. The presence of petroleum hydrocarbon contaminants in the soil and water environments causes significant environmental impacts and poses a substantial hazard to both human and other forms of life in the polluted environments (Sammarco et al., 2013).

Petroleum hydrocarbon pollution is a significant environmental issue that threaten the aquatic environment whether from benzene or other toxic organic materials (Abha and Singh, 2012). Majority of human's depends solely on petroleum as a source of fuel for vehicles, as lubricants and greases, for heating and electricity generation (Oguche et al. 2022). Petroleum hydrocarbons (PHs) are presently regarded as the main source of energy and are substance for distinct manufacturing companies and daily activities. Petroleum hydrocarbon (PHs) are toxic composite to organism and human's in general (Kuppusamy et al. 2020).

Petroleum contamination in the surrounding habitat in water bodies is a considerable source of concern with a deleterious impact on aquatic organisms and human health. Petroleum hydrocarbon contaminated soil may lose their fertility, permeability and water control, petroleum leaching in surface water causes a destructive effect on the aquatic ecosystem. It does not only cause marine contamination but also poison and contaminates the fishing areas and drinking water source.

When petroleum enters the environment through accidental release from industries during production it may percolate into the ground water aquifer and cause contamination, which will lead to health effects (Islam, 2023). According to environmental protection Agency (USEPA) crude oil released into the environment can negatively impact public health and safety by contaminating drinking water, causing fire and explosion hazards (Sakib, 2021). Similarly, oil pollution can diminish air and water quality, and destroy farmlands. Soil contamination by oil is one of the great environmental concerns, and these petroleum pollutions threaten living organisms in the environment and should be removed (Ahmed and Fahruddin 2018).

The aim of this study is to evaluate the impact of total petroleum hydrocarbon and heavy metals in soil, water and selected biotas in Bodo, Gokana Local Government Area, Rivers State. The objectives of the study is therefore, : (i) to determine the heavy metal concentration in surface water and sediments, (ii) to evaluate the total petroleum hydrocarbon (TPH) in surface water and sediments and (iii) to analyze the total petroleum hydrocarbon and heavy metal concentration in some biotas (fiddler crab (*Uca tangeri*), swimming crab (*Callinectes amnicola*) and mudskipper (*Periphthalmus babarus*)

2. Materials and Method

2.1 Description of Study Area

This research work was carried out in Bodo Gokana Local Government Ogoni, Rivers State, Nigeria. It is located between longitude 7.2700820 ^{0}E and latitude 4.6293689 ^{0}N (Figure 1). The main occupation of its indigenes is fishing as a result of their close proximity to the Atlantic Ocean and farming. A rich supply of mangrove forest surrounds it. Bodo is an oil-producing community that hosts pipelines and wellheads belonging to the Shell Petroleum Development Company. Bodo is one of the communities where remediation work has been done to restore the mangrove ecosystem impacted by long-term oil and gas exploration. The Bodo locality have a have a climate which consist of short dry season from October to March and a long wet season which extends from April to October. The study area is located in the Niger Delta region of Nigeria which is one of the most industrialized regions in the entire Gulf of Guinea. The region is identified by large oil and gas activities, oil spillage which have massive impact on aquatic organism and human health. Three sampling stations were identified and selected along the River course. Station I– Goi, Station 2– St Patrick water side and Station 3– St Patrick water side.

Station I (Goi): The open water lies between longitude 4^{0}38'34.914N and latitude 7^{0}16'3678E with an elevation of 8m. it is about 18m for St Patrick water side.

Station 2 (St Patrick water side): The open water station lies between longitude 7'24'38.1N and Latitude 4'63'00.5E with an elevation of 6km above sea level. It is about 4km from Bodo Bridge. It is characterized by high dominance of mangrove.

Station 3 (St Patrick waterside): Comprises of mangrove vegetation which lies between longitude 7'25'39.2N and latitude 4'63'00.5'E with an elevation of 4km above sea level. It is about 6km from Bodo Bridge.

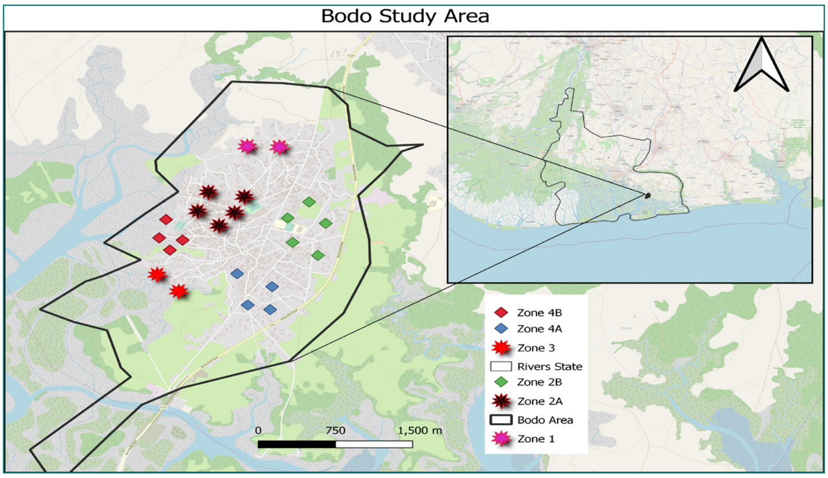

Figure 1A. *Map of study area showing sampling sites at Bodo, Rivers State, Nigeria. Zone 1= site 1, zone 2= site 2 and zones 3 and 4 = sites 3.*

2.2 Sample Collection

Water, sediment and organisms samples were collected from three sampling stations monthly for period of six months between June to December except September.

Water samples: were collected in 1 litre sterile plastic bottle and cocked properly to avoid leakage. Sample bottle were labeled appropriately and transported to the laboratory in a cooler under < 6 °C.

Sediment: Samples were collected using a trowel operated by hand down to a depth of 0.5m, samples collected were sieved to removed debris and excess water, labeled appropriately and transported to the laboratory in a cooler under < 6 °C..

Organisms: 10 fiddler and 10 swimming crabs were collected with a crab net, debris were removed by rinsing thoroughly with distilled water and kept in a container that has tiny opening for ventilation. The crabs samples were identified to the least taxonomic level using taxonomic keys and identified organisms were sorted, and preserved in 10% formalin.

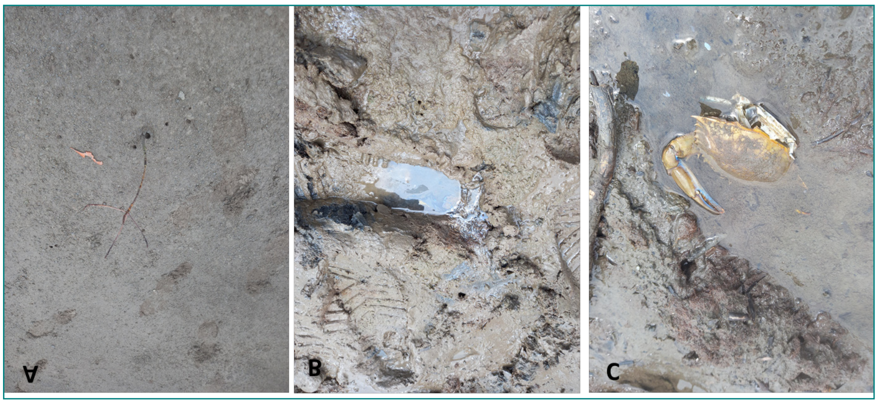

Figure 1B. *Field observations during sampling showing (A) Dead mangrove seedling (Rhizophora Ispp), (b) ground-seeping crude oil and (C) dead water crab (Callinectes amnicola).*

2.3 Determination of Physicochemical Parameters

Soil pH was determined with a Kelway soil tester while the soil compaction was determined with a pocket penetrometer. Soil temperature was determined with a digital dual sensor thermometer to a detection unit of ± 1˚C. The salinity of the pore water soil was determined with a salinity meter (OAKTON Salt 6 Acorn Series). The salinity meter probe was used to test standing water in dug-out holes during low tide. Total organic content (TOC) was determined using the Walkey-Black titrimetric method. The TOC was used to determine the nutrients in the soil. The TOC was determined because soil organic content influences soil texture and composition, which in turn influences mangrove growth. In determining the soil and water chemistry of the study area, the following parameters were analyzed: Total petroleum hydrocarbon (TPH), Lead (Pb), cadmium (Cd), and chromium (Cr) using standard laboratory procedures. It involved the use of a spectrophotometric method using the HACH DR 890 calorimeter (wavelength 420 nm). The samples were crushed, and 2 g of the crushed sample was weighed into a glass beaker. 20 ml of hexane was added, and with the aid of a glass rod, the mixture was homogenized by stirring. Afterward, the sample was filtered in a glass funnel packed with cotton wool, silica gel, and anhydrous sodium sulphate. After this, 10 ml of the filtered organic extract was transferred into a 10 ml sample curve and inserted into the calorimeter. The detection limit for THC is 0.01 mg/l.Heavy metals such as cadmium, chromium, lead, and zinc. These heavy metals were determined using the AAS-Atomic Absorption Spectrometry method.

2.4 Statistical Analysis

An analysis of variance (ANOVA) was conducted since there were multiple samples per block to test whether there was any significant difference in the concentration of hydrocarbon and heavy metals in water, soil, plant and animal samples collected within study plots. Logarithmic transformation of the data was performed to meet assumptions of normality and homoscedasticity (Logan, 2010). Similarly, a post-hoc Tukey's HSD test was done to investigate pair wise mean differences between groups. All analyses were performed in R statistical environment, 3.0.1 (R Core Team, 2013). To determine the heavy metal concentration between surface water and sediment, it was hypothesized as follows: H_o: there is no significant difference in the heavy metal concentration between the surface water and sediment. H_a: there is a significant difference in the heavy metal concentration between the surface water and sediment.

3. Results

3.1 Physico-Chemistry of Study Area

Water: The background physico-chemistry of the study site reveal the following ranges for water temperature (27.4–30.2 °C), pH (8.0–81), DO (5.1–5.8 mg/l), BOD (1.42–2.87 mg/l) and conductivity (10490–12010 µ/cm) (Table 1).

Table 1. *Physico-chemical parameters of water at study sites in Bodo, Rivers State, Nigeria.*

Parameters	Site 1	Site 2	Site 3	WHO /FEPA† Limits
Temperature, °C	29.6	30.2	27.4	32
pH	8	8.1	8	6.0-9.0
Conductivity (µ/cm)	12010	10490	10520	900
DO (mg/l)	5.1	5.8	5.4	4.0
BOD (mg/l)	2.86	2.87	1.42	50
COD (mg/l)	4.29	4.31	2.13	20
Total Alkalinity (mg/l)	200	160	170	100
Total Hardness (mg/l)	2040	1870	1880	100
TPH (mg/l)	1.16	0.65	0.95	500
TDS (mg/l)	6603	5770	5790	500 (as total solids)

†FEPA (1991)'Key: DO= Dissolved oxygen, BOD=Biological oxygen demand, COD=Chemical oxygen demand

Sediment: The background physico-chemistry of the study site reveal the following ranges for sediment- pH (7.0–7.3), conductivity (4650–2880 µ/cm) (Table 2).

Table 2. *Physico-chemical parameter of sediment at study sites in Bodo, Riverts State, Nigeria.*

Parameters	Site 1	Site 2	Site 3	WHO Limits
pH	7	7.3	7.1	NS
Conductivity (µ/cm)	4650	2880	4580	NS
CEC (meq/100g)	17.73	13.507	17.623	NS
TOC (%)	3.081	3.198	2.574	NS
TPH (mg/kg)	213.17	1082.3	172.8	50
Moisture Content (%)	58.25	34.19	51.76	NS
Sand (%)	78.7	76.8	77.84	NS
Silt (%)	4.42	4.5	4.63	NS
Clay (%)	16.88	18.7	17.53	NS
Particle Size Distribution	SL	SL	SL	NS

Where SL=Sandy Lomy, SS=Sandy Soil, NS=Not Specified)

3.2 Heavy Metal Concentration in Surface Water and Sediment

The ANOVA result show that P<0.05 ($F_{1, 142}$ = 31.75, P<0.001, Figure 2), which means that there is significant difference in the heavy metal concentration between the surface water and sediment. The result reveal that the concentration of heavy metals is higher in sediments than in surface water.

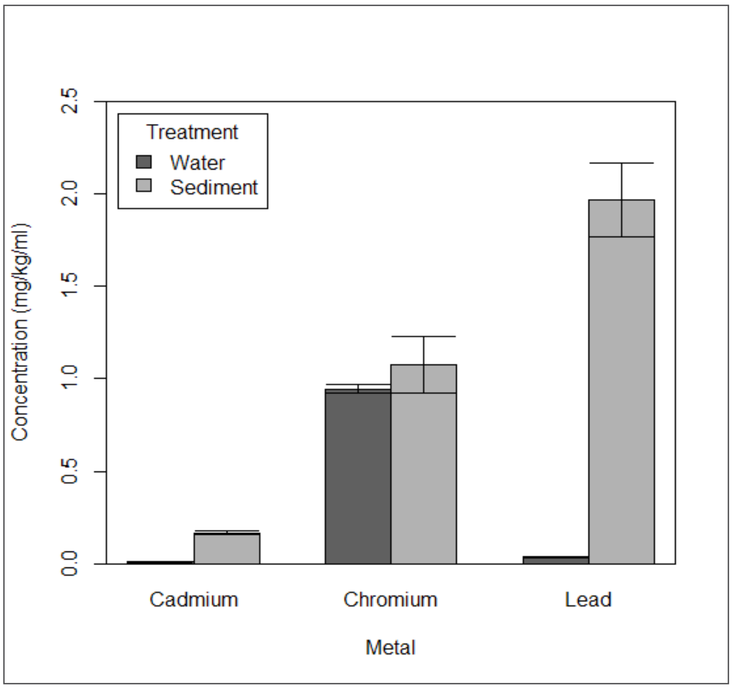

Figure 2. *Bar graph of heavy metal concentration in surface water and sediment at Bodo Creek, Rivers Sate, Nigeria (±SE).*

3.3 Seasonal comparison of heavy metal concentration

The ANOVA result show that P>0.05 ($F_{1, 142}$ = 0.98, P>0.001, Figure 3), which means there is no significant difference in the heavy metal concentration between the dry and wet seasons.

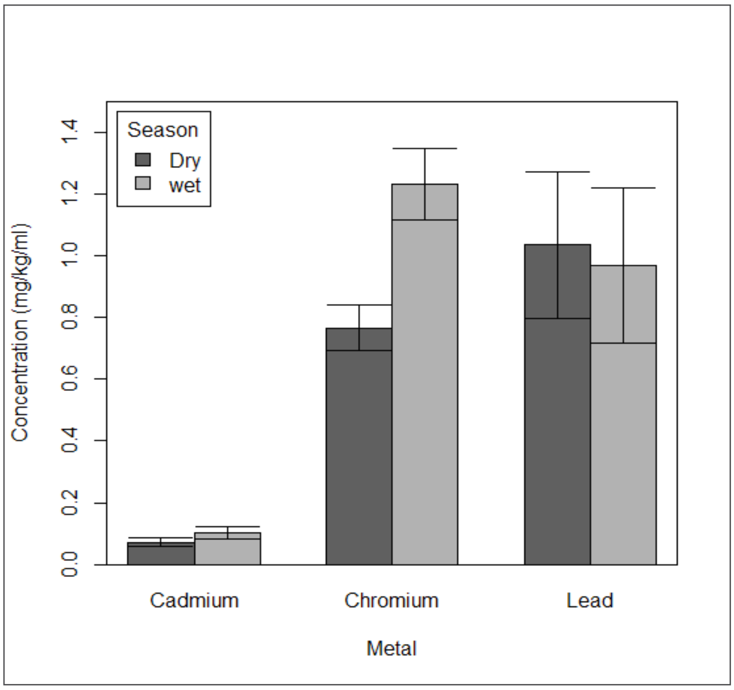

Figure 3. *Bar graph of heavy metal concentration in dry and wet seasons at Bodo Creek, Rivers Sate, Nigeria (±SE).*

3.4 Monthly Comparison of TPH

The ANOVA result show that there is significant difference in TPH concentration between surface water and sediment ($F_{1, 38}$ = 366.7, P<0.001, Table 3, Figure 4). In contrast there is no significant difference in months ($F_{1, 32}$ = 0.14, P>0.05, Figure 4)

Table 3. *Mean TPH concentration in surface water and sediment at Bodo Creek, Rivers State, Nigeria (±SE)*

Samples	Mg/kg/ml							
	June	July	August	September	October	November	December	January
Water	11.00±0.40	11.36±0.68	10.85±0.53	11.63±0.70	0.74±0.07	0.71±0.06	0.74±0.06	0.77±0.12
Sediment	1130.36±0.51	1163.29±42.10	1158.92±29.05	1159.20±34.22	751.77 ±172.51	742.75 ±182.94	762.89 ±173.06	767.60±185.81

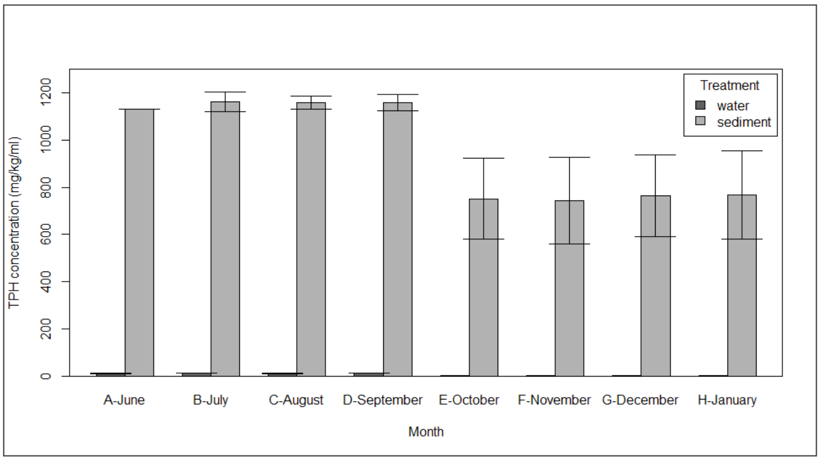

Figure 4. *Mean total petroleum hydrocarbon (TPH) concentration at Bodo Creek, Rivers State, Nigeria (±SE).*

3.5 Physico-Chemistry of Biota

Four different mangrove-associated species namely: fiddler crab (*Uca tangeri*), water crab (*Callinectes amnicola*), and mudskipper (*Periophthalmus barbarus*) were analyzed in the laboratory to determine the impact of hydrocarbon pollution on biota (Table 4). The ANOVA result reveal that there is a significant difference in chemical concentration in the Biota ($F_{3, 36} = 8.21$, $P < 0.001$). Higher concentration of Cadmium and Chromium was found in *c. amnicola* whereas *U. tangeri* has the highest cadmium concentration while *P. babarus* has the highest concentration of manganese (Table 4). The Tukey HSD test shows that fiddler crab has the most significant different concentration from the FEPA limit (Table 5).

Table 4. *Mean concentration of total petroleum hydrocarbon and heavy metal in selected biota at Bodo, Rivers State, Nigeria.*

Parameters	Fiddler crab (*Uca tangeri*)	Water crab (*Callinectes amnicola*)	Mudskipper (*Periophthalmus babarus*)	‡FEPA Limits
TPH	0.001	0.001	0.001	50
Cd	2.07	2.36	1.21	0.8*
Cr	0.001	2.99	0.001	100
Pb	2.28	2.14	0.67	85
Mn	0.001	8.78	45.54	NS

above limits; ‡ FEPA (1991)

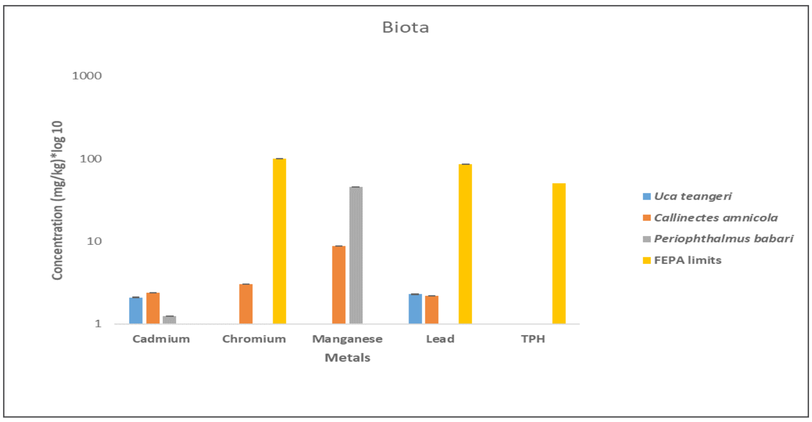

Figure 5. *Concentration of total hydrocarbon and heavy metals in selected biota at Bodo, Rivers State, Nigeria (±SE). The Cadmium and Manganese concentrations are above the FEPA limits.*

Table 5. *Tukey HSD test for chemical concentration in biota at Bodo, Rivets State, Nigeria*

	diff	lwr	upr	p adj
fiddler-control	-46.6561	-75.6247	-17.6876	0.000619*
mudskipper-control	-38.0344	-67.003	-9.06586	0.005992*
swimming-control	-44.2477	-73.2163	-15.2792	0.001188*
mudskipper-fiddler	8.6217	-20.3469	37.59028	0.853224
swimming-fiddler	2.4084	-26.5602	31.37698	0.995967
swimming-mudskipper	-6.2133	-35.1819	22.75528	0.93814

4. Discussion

High total dissolved solids (TDS) in water are caused by the dissolution of soluble materials in water, which may be organic or inorganic matter. The electrical conductivity signifies the presence of hydrogen ions, and it is approximately proportional to the TDS content. The concentration of TDS above international standards will harm aquatic organisms' health. Total alkalinity is when the pH is greater than 4.5; the hydrocarbon content of the water influences it. The hardness of the water is caused by the Ca^{2+} and Mg^{2+} content. Acidic components of crude oil seep into the shore soil, leading to the release of calcium and magnesium products, which cause the hardness of the water.

The high concentration of Chromium, and Lead in the surface water indicates the presence of hydrocarbon products such as crude oil. Heavy metals are detrimental to people's health because of the bioaccumulation of toxic components into the bodies of aquatic organisms, which are later transferred to humans through the food chain. Furthermore, the presence of high TPH concentration (742.75±182.94 to 1163.29±42.10 mg/kg) in sediment above WHO standards strongly points to the presence of developing or recurring pollution caused by a concatenation of oil spills in the study area in the recent past. The presence of high concentrations of TPH in sediments above WHO Limits (Table 2) signifies a polluted environment. Many coastal soils were found saturated with crude oil during the fieldwork. The crude oil periodically seeps into the surface water to contaminate it, leading to higher levels of metallic components (E.g., Site 1). Observations were also made of dead mangrove seedlings (Figure 1B), which must have been planted during the remediation work. Cadmium concentration was particularly above the international standards in both soil and biota (Table 4). Cadmium is classified as a toxic metal substance that will negatively impact the health of the people whose occupation is fishing and farming. Harmful effects of Cadmium include sterilization of farm animals, heart disease in humans and damage to the kidney and liver, and bone deformation (WHO, 1983; UNEP, 1986). Aromatic hydrocarbons (E.g. PAH) has carcinogenic and teratogenic effects on humans.

The water, soil, and biota test results shows that the study area is polluted by crude oil. The remediated regions are re-polluted by crude oil spills. Some sites studied (e.g., Site 1, Figure 1B) have soil saturated with crude oil, which bubbles out gradually onto the surface water when dug. Fingerprints of oiling activity were found everywhere visited, such as the pungent smell of crude oil, dead swimming (*A. amnicola*) (Figure 2C) and fiddler (*U. tangeri*) crabs lying on the soil surface, shiny mangrove leaves indicating oiling, and rows of dead red mangrove (*Rhizophora*) seedlings whose relics were still clearly seen standing to show a recent planting event.

5. Conclusion

The area is polluted as a result of past or recent oiling activities, which led to the high concentration of chemical components in soil and biota. The contamination of the environment is detrimental to the local population who depend on the sea food as their source of livelihood. There should be constant monitoring of the soil, water and biota to detect increase in chemical components across the food chain. Activities leading to crude oil spills (pipeline leakage, waste disposal and artisanal refinery) should be stopped to prevent the re-oiling of remediated areas.

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Conflicts of Interest

The author declares there is no conflict of interest.

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