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Determination of PAHs and BTEX in Soil and Crops (Cocoyam and Cassava) of Crude Oil Impacted Community, Mogho Gokana, Nigeria

O. G. Echem[1], I. A. Kalagbor[1], G. B. Lucky[1]

[1]Department of science Laboratory Technology, Ken Saro-Wiwa Polytechnic, Bori, Rivers State, Nigeria

Abstract: The aim of this study is to determine the impact of crude oil spillage on soil and harvested tuber crops (cocoyam and cassava) in Mogho Community. Polycyclic aromatic hydrocarbons (PAHs), benzene, toluene, ethylbenzene, xylene (BTEX) were investigated using Gas Chromatography – Flame Ionization Detector. Tuber crops and soils from crude oil impacted area of Mogho Community were used as the sample; while soil not impacted by crude oil were collected from Bori was used as the control. The results obtained for PAHs showed mean concentration of 0.035mg/kg for polluted soil; 0.001mg/kg for cassava, and 0.005mg/kg for cocoyam harvested from the polluted soil while the unpolluted soil (control) had a mean concentration of 0.002mg/kg. The mean concentration of BTEX for the samples was <0.001 which is below detection limit. The presence of PAHs in samples was found to be both low molecular weight and high molecular weight. The PAHs found in the polluted soil was higher compared to that of the unpolluted soil. The concentration of PAHs found in samples, exceeds the recommended permissible limit of WHO standard, which is (0.0001mg/kg). These results reveal that crude oil pollution is responsible for the presence of PAHs in soils and tuber crops like cassava and cocoyam which are frequently consumed in our localities. Government and oil companies should employ mitigating measures to deal with pipeline vandalization and oil spillage in this area.

Keywords: PAHs, BTEX, Soil, Tuber Crops, Crude Oil

1 Introduction

Crude oil is a naturally-occurring unrefined petroleum product composed of hydrocarbon deposits and other organic matter that when refined, produce other products like diesel, gasoline, heating oil, jet fuel, kerosene and literally other products called petrochemicals. Crude oil has profound impact on the world civilization than any single natural resource in recorded history. Oil has become decisive element in defining politics, rhetoric and diplomacy of states. All over the world, the lives of people are affected and destiny of nations has been determined by the result of oil explorations.

Soil is the most valuable component of farming. The ecosystem and environmental sustainability largely depends on soil management. Sustainable use of agricultural soil on which plants depend is absolutely necessary for agricultural productivity. Soil, when polluted by crude oil and other petroleum products becomes a problem to agricultural productivity and thus creates poverty and hunger among the people (Adenipekun and Kassim, 2006; Adenipekun and Kassim, 2009). Oil pollution in agricultural soil in whatever form is toxic to the plant and soil micro-environment. It has been observed by several researchers that crude oil affects agricultural soil and this in turn affect the physiological, ecological and anatomical development of plants grown on such soils. (Anoliefo and Vwioko, 1995; Udo and Fayemi, 1975). The presence of crude oil in the plant-soil micro-environment affects normal soil chemistry such that it reduces the release of nutrient uptake as well as the amount of water available to the plants. The decrease in heights and growth of plants in crude oil polluted soil may be due to non-availability of adequate uptake and mobility. Crude oil pollution on soil changes the physical and chemical properties of soil and its structure (Chi and Krishnamurthy, 1995). These compounds are largely responsible for altered fertility of soil. Affected soils lose their biological activity and many require up to ten years to recover it (Wyszkowska *et al.*, 2001).One of the indices of loss of biological activity of soils as a result of crude oil pollution is the reduction or inhibition of microbial activity.

Tuber crops also called roots crops are plants that are grown for their modified, thickened root or stem which generally develop underground. Tuber crops provide a substantial part of the world's food supply, and are also an important source of animal feed and industrial product. On a global basis approximately 45 percentage of tuber crop production is consumed as food, with the remainder used as animal feed or for industrial processing for product (starch, distilled spirit and a range of minor products). The consumption of tuber crops as food in developed

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O. G. Echem Correspondence)
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countries is considerably smaller than it is in developing countries (Fisme *et al.*, 2002)

- Cocoyam (*Colocasia esculenta*) is herbaceous perennial plants belonging to the family Araceae and is grown primarily for their edible roots, although all parts of the plants are edible. Cocoyam is cultivated as food crop belonging to either the genus colocusia or the genus xanthosoma. It is swollen underground, from which a few large leaves emerge.
- Cassava (*Manihot esculenta)* is a dicotyledonous plant belonging to the Euphorbiaceae family. It is a perennial woody shrub which grows in tropical and subtropical areas of the world. The crop is a root tuber crop (IITA, 2005). Cassava being a major staple food in Nigeria is known to grow in various adverse environmental conditions including crude oil contaminated soil which will equally affect the nutritional status of the plant (Ogbuechi and Akonye, 2008).

PAHs (Polyclyclic Aromatic Hydrocarbon) generally have low degree of acute toxicity to humans. Some studies have shown non carcinogenic effects that are based on PAH exposure (Gupta *et al.*, 1993). After chronic exposure, the non-carcinogenic effect of PAHs involve primarily the; Pulmonary, Gastrointestinal, Renal, and Dermatologic system Many PAHs are slightly mutagenic or even non-mutagenic invitro. However, their metabolites or derivatives can be potent mutagens (Gupta *et al.*, 1993). The effects on human health will depend mainly on the amount one is exposed to (or concentration), the innate toxicity of the PAHs and whether exposure occurs via inhalation, ingestion or skin contact, exposure to contaminated soil/dust, and from inhalation of PAH vapours. Tilling of dry soil can result in ingestion of small but measurable amounts of soil. An occupational exposure to high levels of pollutant mixtures containing PAHs has resulted in symptoms such as eye irritation, nausea, vomiting, diarrhea and confusion. Long-term studies of workers exposed to mixtures of PAHs and other workplace chemicals have shown an increased risk of skin, lung, bladder and gastrointestinal cancers. These studies have also reported asthma-like symptoms, lung function abnormalities, chronic bronchitis and decreased immune function (Public Health Fact Sheet Polycyclic Aromatic Hydrocarbons (PAHs): Health effects, 2010).

The acronym “BTEX” actually refers to four separate chemicals with similar properties. They are Benzene, Toluene, Ethyl-benzene, and Xylene. BTEX are naturally occurring components of crude oil meaning that they are found in small concentrations in refined oil products such as diesel, gasoline, and aviation fuel. BTEX are toxic to humans and their removal from polluted environment is of special interest. They are in class of chemicals known as Volatile Organic Compounds (VOCs) (Srijata and Pranab, 2011). Exposure to BTEX can be through drinking of contaminated water (ingestion), breathing contaminated air from pumping gas or from water through showering of laundering (inhalation) from spills on the skin. Short term exposure to gasoline and its components such as benzene, toluene and xylenes has been associated with skin and sensory irritation, central nervous system – CNS problems (tiredness, dizziness, headache, loss of coordination) and effects on respiratory system (eye and nose irritation) (Srijata and Pranab, 2011). Prolonged exposure to these compounds can also affect the kidney, liver and blood systems. Benzene is known to be carcinogenic and has also been shown to cause blood disorders and to impact the central nervous system and the reproductive system. Toluene may affect the reproductive system and central nervous system. Ethyl benzene and xylene may have respiratory and neurological effects (BTEX.cfm, 2011). BTEX can produce neurological impairment, and benzene can additionally cause hematological effects which may ultimately lead to plastic anemia and development of acute nyelogenous leukemia (ATSDR. 1995).

II. MATERIALS AND METHOD

Materials: Cassava, Cocoyam and crude oil impacted Soil were collected from Mogho Community, one of the communities in Ogoni land, Niger Delta region of Nigeria.

Collection of Tubers: Tuber crops (cassava and cocoyam) were freshly harvested in the farmland within the study area.

Collection of Soil Samples: Crude oil polluted soil sample was collected few meters away from the spot where the tuber crops were harvested. The sample was stored in a nylon bag.

The control soil sample was also collected from an area free of crude oil exploitation and stored in a nylon bag. These soil samples were transported to the laboratory for processing and analysis.

Preparation of Tuber crops: The harvested tubers (cassava and cocoyam) were peeled using knife to remove the coat and washed with distilled water. The peeled samples were sliced and divided into two portions, one portion for PAHs analysis, and the other for BTEX analysis. For PAHs analysis, 20 grams of each sample were blended into slurry form before analysis. The same procedure was used for the portion for BTEX analysis.

Soil Preparation: 20 grams of the soil samples collected were sieved to remove stones and debris and were later divided into two portions, one portion for PAHs analysis and the other for BTEX analysis. The soil samples for PAHs and BTEX analysis was also crushed, sieved and stored for analysis.

Determination of PAHs and BTEX in Tuber Crops

Three experimental processes were involved in the determination of PAHs and BTEX in the samples.

1) Extraction

2 grams of prepared tuber samples (cassava and cocoyam) were weighed into two different clean extraction containers. 10 ml of extraction solvent (pentane) was added into the samples, mixed thoroughly and allowed to settle.

The mixtures were carefully filtered into clean solvent extraction bottles using filter paper fitted into Buchner funnels. The extracts were concentrated to 2 ml and then transferred to cleanup/separation.

2) Gas Chromatographic Analysis

Gas Chromatography (GC) – Flame Ionization Detector (HP 5890 series 11), Blender (Masterchef, Model MC-Y44B), Knife, Filter Paper, Extraction bottles, Hypodermic syringe, Buchner funnel, 10ml Graduated cylinder.

The column concentrated aliphatic fractions were transferred into labeled glass vials with Teflon or rubber crimp caps of GC analysis. 1 ml of the concentrated sample was injected by means of hypodermic syringe through a rubber septum into the column. Separation occurs as the vapour constituent partitions between the gas and liquid phases. The sample was automatically detected as it emerged from the column (at a constant flow rate) by the FID detector whose response is dependent upon the composition of the vapour.

III. Results And Discussion

The results for the determination of PAHs and BTEX in soil and tuber crops are presented in Table 1-2 and Fig 1-2.

Table 1: PAHs and BTEX values of soil and tuber crops sample in comparison with WHO standard.

S/N	SAMPLES	PAHs (mg/kg)	BTEX (mg/kg)
1	Cassava	0.001	<0.001
2	Cocoyam	0.005	<0.001
3	Polluted Soil	0.035	<0.001
4	Soil (control)	0.002	<0.001
5	WHO	0.0001	0.01

Source: WHO (1993)

Table 2: PAHs constituents and levels in soil and tuber crops

	(PAHs concentration in mg/kg)			
PAHs	Cocoyam	Cassava	Polluted Soil	Soil (control)
Napthalene	ND	7.35×10^{-6}	4.24×10^{-5}	ND
2-methyl Naphthalene	ND	5.75×10^{-6}	2.53×10^{-4}	ND
Acenaphthylene	ND	ND	3.26×10^{-4}	ND
Acenaphthene	1.69×10^{-5}	2.42×10^{-7}	1.39×10^{-4}	ND
Fluorene	ND	3.76×10^{-6}	4.95×10^{-4}	ND
Phenanthrene	5.67×10^{-5}	ND	3.42×10^{-4}	ND
Anthracene	6.35×10^{-5}	8.64×10^{-6}	2.65×10^{-4}	4.49×10^{-5}
Fluorenthene	3.30×10^{-4}	ND	3.22×10^{-3}	2.05×10^{-4}
Pyrene	9.96×10^{-5}	ND	8.27×10^{-4}	ND
Benzo (a) Anthracene	ND	ND	7.54×10^{-4}	ND
Chrysene	1.04×10^{-3}	ND	5.24×10^{-3}	ND
Benzo (b) fluoranthene	2.81×10^{-4}	ND	2.00×10^{-3}	ND
Benzo (k) fluoranthene	1.88×10^{-4}	ND	1.45×10^{-3}	6.28×10^{-4}
Benzo (a) pyrene	4.36×10^{-4}	1.89×10^{-4}	2.14×10^{-3}	2.07×10^{-4}
Indeno(1,2,3-cd)pyrene	1.32×10^{-4}	6.28×10^{-5}	8.74×10^{-4}	7.54×10^{-5}
Dibenz (a,h) anthracene	1.62×10^{-4}	4.85×10^{-5}	1.17×10^{-3}	7.74×10^{-5}
Benzo (g,h,i) perylene	1.65×10^{-4}	2.71×10^{-4}	1.53×10^{-2}	9.16×10^{-4}

Where ND= not detected.

The result of the constituent of polycyclic aromatic hydrocarbon (PAHs) and BTEX found in soil and tuber crops harvested in Mogho, Gokana is presented in Table 1. The values of PAHs in the study area were 0.002 mg/kg, 0.035mg/kg, 0.001mg/kg, and 0.005 mg/kg for unpolluted soil, polluted soil, cassava and cocoyam respectively. BTEX was below detection level (<0.001) in the samples. The result shows that the concentration of PAHs in crude oil polluted soil was higher than that of the unpolluted soil. PAH concentrations were higher in cocoyam than in cassava.

The various PAHs constituents found in cocoyam were Acenaphthene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Chrysene, Benzo (b) fluoranthene, Benzo (k) fluoranthene, Benzo (a) pyrene, Indeno (1,2,3-cd) pyrene, Dibenz (a,h) anthracene, Benzo (g,h,i) perylene, Dibenz (a,h) anthracene, and Benzo (g,h,i) perylene. For cassava, Naphthalene, 2-methyl Naphthalene, Acenaphthylene, Fluorene, Anthracene, Benzo (k) fluoranthene, Benzo (a) pyrene, Indeno (1,2,3-cd) pyrene, Dibenz (a,h) anthracene, Benzo (g,h,i) perylene were found. Naphthalene, 2-methyl Naphthalene, Acenaphthylene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benz (a) anthracene, Chrylene, Benzo (b) fluoranthene, Benzo (k) fluoranthene, Benzo (a) pyrene, Indeno (1,2,3-cd) pyrene, Dibenz (a,h) anthracene, Benzo (g,h,i) perylene were found in the polluted soil; whereas only Anthracene, fluoranthene, Benzo (a) pyrene, Indeno (1,2,3-cd) pyrene, Dibenz (a,h) anthracene, Benzo (g,h,i) perylene were found in the unpolluted soil as shown in Table 2 and the composite pattern of PAHs and BTEX distribution in soils and tuber crops as shown in Fig 1. The GC-FID chromatograph is presented in Fig. 2.

From the results, cocoyam tuber did not ingest detectable amount of Napthalene, 2-methyl Naphthalene and Fluorene (these were detected in cassava), Acenaphthene and Benzo(a) Anthracene (not detected in both tuber crops under study). It was further observed that Phenanthrene, fluorenthene, Pyrene, Chrysene, Benzo(b) fluoranthene, and Benzo(k) fluoranthene were not detected in cocoyam but in were detected in cassava tuber.

This suggests that though both crops are tubers, they differ significantly in their bioactive scavenger constituents.

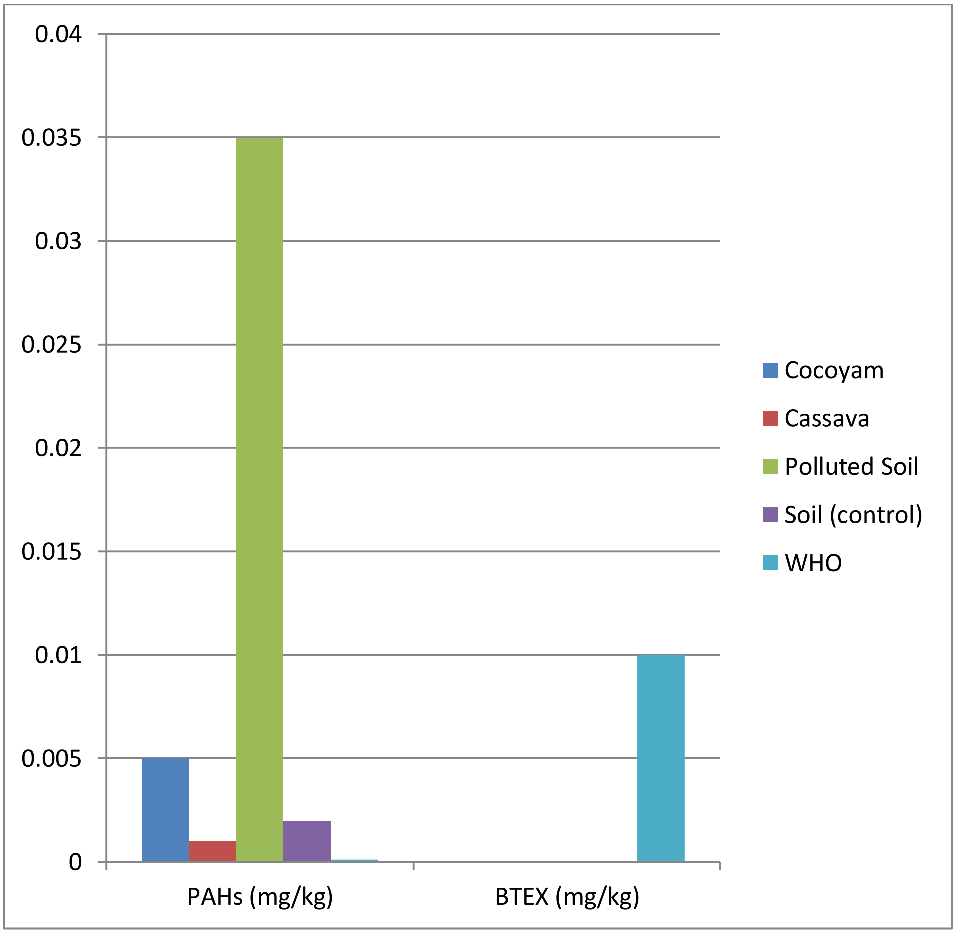

Figure 1: Composite pattern of PAHs and BTEX values in oil and tuber crops sample

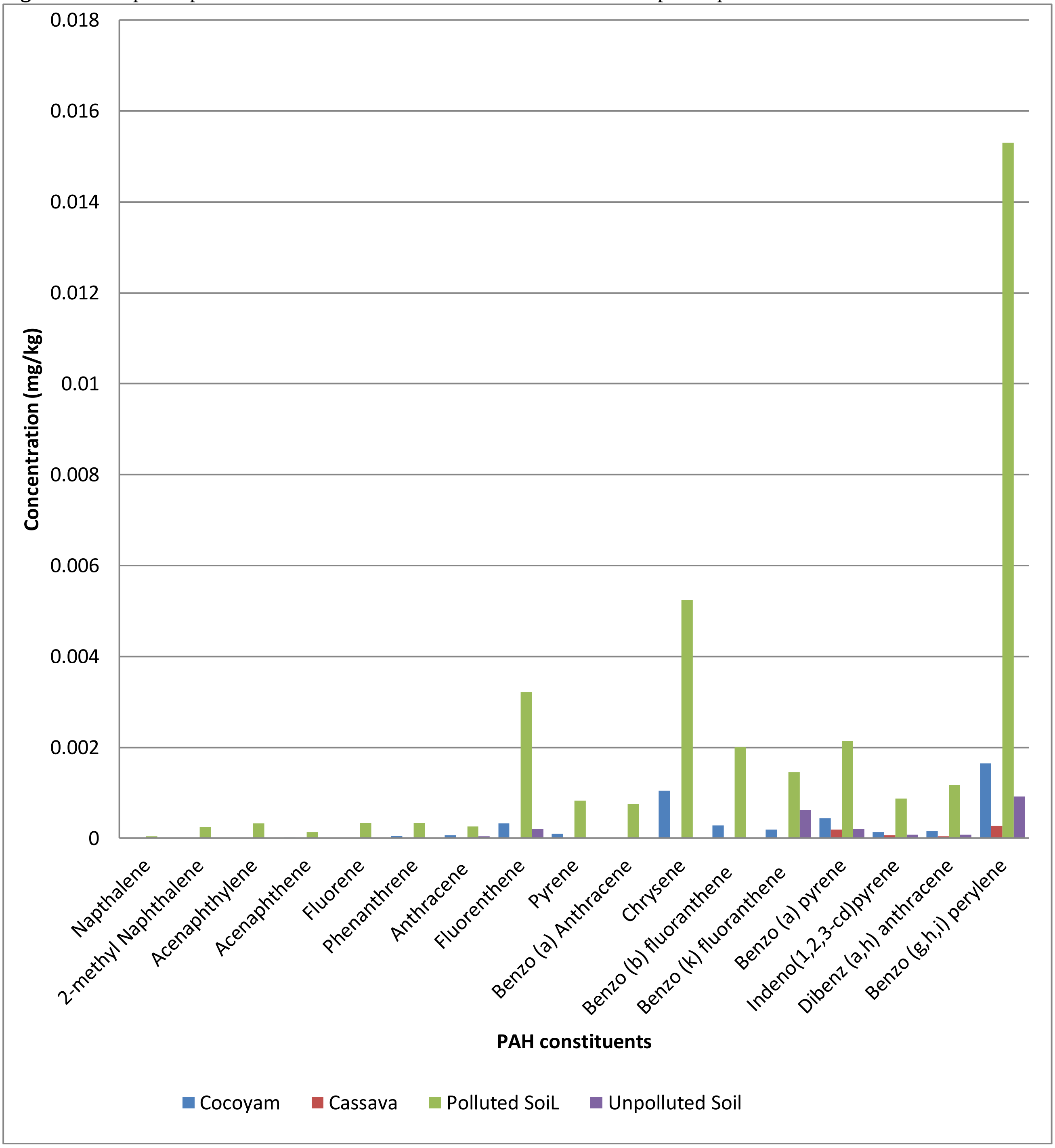

Fig 2: GC-FID chromatogram for PAHs distribution in soils and tuber crops.

IV. Conclusion

From the results, it can be concluded that PAHs were present in the soil and tuber crops from crude oil impacted community of Mogho Gokana, Nigeria. The observed levels of persistent PAHs (Benzo (a) anthracene, Benzo (k) fluoranthene, Benzo (a) pyrene,benzo(b) fluoranthene and Chrysene) in soil and tuber crops harvested in these crude oil impacted community is obviously a cause for concern as these contaminants may make the food crops unsafe for human, livestock and industrial uses and if crude oil pollution in these areas is not checked, continued accumulation of these pollutants may render the soils unsuitable for agricultural purposes apart from endangering the health of the inhabitants that depend on these cultivars for food.

Recommendation

Based on the findings of this study, we recommend that the government and oil companies should employ mitigating measures to deal with oil spillage in this area and that further research work should be carried out at the study area.

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