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Distribution of Heavy Metals and Total Petroleum Hydrocarbons in Soil and Cassava (*Manihot Esculenta***) around Omoku, Rivers State, Nigeria**

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Abstract

Heavy metals and total petroleum hydrocarbon pollution is a worldwide phenomenon which results from both natural and anthropogenic activities. This has resulted in several health and physiological problems. This study investigated the level of heavy metal pollution and total petroleum hydrocarbon content in cassava (*Manihot esculenta*) and soil of Omoku (Obagi, Obrikom, Ebocha) and a control point in Rivers State. Cassava (*Manihot esculenta*) and soil samples from different locations were analysed for heavy metals and total petroleum hydrocarbon using atomic absorption spectrophotometer and GC-FID. The data obtained were further subjected to index models (contamination factor, PLI and bioaccumulation factor) of the heavy metals. The data acquired showed that the mean levels of heavy metals (Cr, Cd, Pb, Cu, Fe and Ni) in cassava samples determined ranged from $5.17\pm0.04 - 7.43\pm0.00$ for Cr, $0.05\pm0.00-$ 1.41±0.00 forCd, 1.70±0.00 – 3.62±0.00 for Pb, 5.86±0.00 – 8.54±0.02 for Cu, 66.032±0.13 – 87.49±0.07 for Fe and 1.723±0.05– 5.801±0.01 for Ni.In soil samples, it was 9.38±0.00– 9.63±0.05 for Cr, 2.61±0.01– 6.78±0.01 for Cd, 7.65±0.00 – 8.56±0.03 for Pb, 7.97±0.01– 8.74±0.02 for Cu, 67.17±0.00 – 87.51±0.08 for Fe and 7.48±0.07 – 8.72±0.05 for Ni. The mean levels of total petroleum hydrocarbon determined in cassava (*Manihot esculenta*) include 442.00±16.26, 320.67±0.88 and 255.33±6.39 mg/kg for Obagi, Obrikom and Ebocha respectively. In the soil, they include;1095.00±3.00, 895.67±0.88 and 647.33±6.67 mg/kg for Obagi, Obrikom and Ebocha respectively. The results were compared with the standard limits, and it was observed that some of the heavy metals were above the limit, and others were below it. The Pollution load index was also used to ascertain the levels of soil pollution by heavy metals, indicating that all the locations where sampling took place were unpolluted with heavy metals. The highest bioaccumulation factor of the heavy metal in cassava (*Manihot esculenta*) was Fe and the lowest was discovered to be Cd. It is therefore recommended that emissions from companies into the environment should be minimized.

Keywords: Heavy Metals, Total Petroleum Hydrocarbon, Soil and Cassava

Introduction

Human activities, which have led to the release of pollutants into the atmosphere pose a huge challenge to soil nutrients which in turn influences the quality of agricultural products within any locality. These activities are both conscious and unconscious disposal of waste from domestic and industrial waste injected into the environment. This unlawful disposal of industrial waste is said to be because most companies refuse to follow the laid down safety and environmental best practices of proper treatment of waste before injecting them into our environment and where this is in place, individual staff of such companies do this out of negligence. The sabotage of oil exploration and exploitation companies which includes oil pipeline vandalism resulting in spillage is one of the major sources of environmental pollutionin the oil-rich Niger Delta region of Nigeria (Albert et al., 2019). The consideration of the total petroleum hydrocarbon (TPH) is said to be important when environmental pollutants are being discussed, owing to the toxic nature of the components that are classified to have formed it. Total petroleum hydrocarbon (TPH) is however said to be a terminology that is commonly used to describe the quantity of petroleum-based hydrocarbon extracted and quantified by a particular method in an environmental setting. These components of total petroleum hydrocarbon (TPH) released to our environments are said to be organic compounds because the components contain mainly hydrogen and carbon. One has to consider that the effluent from oil exploration companies is treated with inorganic components that can also be released into the soil environment (Sangeetha et al., 2016). These inorganic components are summarized to be known as heavy metals. The discharge of these heavy metals that are associated

with a constituent of oil drilling fluid has also in recent times raisedthe environmental concern to the populace in various vicinities where these oil exploration activities are being carried out. The term or phrase heavy metal is used to describe a collection of metals as well as metalloids with an atomic density greater than five grams per cubic centimetre. Heavy metals are said to naturally coexist with other earth crust components but are grouped as an environmental contaminant due to their non-degradable nature (Sangeetha et al., 2016).

Cassava which originally was cultivated by Latin American Indian indigenes have been in existence for over 4000 years and was introduced by the Portuguese in about the sixteenth century to Africa. Nigeria has also recorded a great feast in the production of cassava as they happen to be the largest cultivator of this crop which has also become one of the most consumed staple food for her citizens. It will be imperative to state that almost all the parts of the cassava crop are usefulin one way or the other as they could be used for the preparation of fufu, garri, flour, tapioca, animal feed, glucose and all-purpose starch. This has made the crop a potential GDP enhancer to Nigeria as it is ranked among the crops that contribute the 85 percent of thecontribution of crops to Nigeria's GDP (Jackson & Chiwona‐Karltun, 2018). Cassava plant is one of the most cultivated agricultural products in Omoku Metropolis in Rivers State because it is used for the production of the most consumed food in Nigeria and Africa at large as well as one of the major sources of agricultural income for a good number of farmers that dwell in the land. However, environmental pollution in Omoku Metropolis in Rivers State where both oil exploration and exploitation activities are being practised may have affected the yield of cassava produce and many other agricultural products cultivated in the area. It is no longer a hypothetical statement to say that the development of the agricultural sector is the way out of Nigeria's economic crisis as cassava products are being exported to another part of the world (Raimi et al., 2021). Cassava products as we all know being cultivated and yield maximally in the south-south region of Nigeria and Omoku in Rivers State is not exceptional, but the presence of these oil exploration and exploitation activities in this region has negatively influenced the nutritional value of this most sourcedfood crop. These activities of oil exploration and exploitation companies in Rivers State, precisely Omoku may have polluted the environment with petroleum hydrocarbon waste products as well as heavy metals such as Co, Cu, Fe, Mn, Ni, Zn etc (Raimi et al., 2021).

It is important to note that cassava which is scientifically known as *Manihot esculenta* is a perennial cash crop that originated in tropical America where it was cultivated by the indigenous Indians and was later introduced to Africa by the Portuguese in the sixteenth century. The establishment of cassava crops as a stable food crop has been since the 19th century and has made its cultivation and consumption in many developing regions of the world more prevalent as it has a large yield and relative resistance to disease and pests (Parmar et al., 2017). It has also been reported that Nigeria which is the largest producer of cassava in the world of which approximately 67 percent of the overall national output of cassava comes from the oil-rich Niger Delta area, has not been able to compete with Brazil, Thailand and Indonesia in the international market as Thailand and Indonesia have taken the lead in the world trade on cassava as at today. This may be because over 90 percent of the cassava produced in our country Nigeria is being consumed as food since it seems to be the cheapest and readily available source ofenergy, while the barely 10 percent remaining are utilized for industrial purposes. This no doubt is because an average Nigerian will seek stomach settlement before seeking how to create material for industrial use. Cassava plants have health benefits because of the presence of glucose, vitamins, iron, calcium, and other nutrients in the diet. The presence of heavy metals contaminants happens to be one of the most significant aspects of food quality assurance. Cassava has been said to be the major source of staple food to several families in tropical Africa region, where Nigeria is the largest producing nation in the world cultivates cassava and processes them in a subsistent farming mode operated by smallholders in Nigeria (Kigigha et al., 2018).

The media in which cassava is cultivated such as the soil have been reported to be the main sources of heavy metals and TPH that are absorbed using roots which can lead to the destruction of animal or human physiological functioning through the food chain. Cassava helps us to alleviate the continuous food insecurity, unemployment challenges and income generation for local farmers in Nigeria of which Omoku Metropolis is not excluded. This study, therefore, evaluates the concentration of TPH and heavy metal in soil and cassava crop harvested from Omoku Metropolis as this will also be able to deduce if cassava contamination with heavy metals correlates with the presence of TPH in soil samples. The government as well as the private sector have become more interested in curbing the continuously increasing pollution of soils with heavy metals and petroleum hydrocarbon contaminants asthey have no doubt affected the yield and nutrition values of agriculturalproduce. This has also led to the evaluation of the allowable petroleum hydrocarbon concentration in soil as stated by the Department of Petroleum Resources, (DPR)

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and intervention values, Shell Petroleum Development Company, (SPDC) and Environmental Guidelines and Standards for Petroleum Industry in Nigeria as 50 ppm, 300 ppm and 500ppm respectively (Okereke et al., 2020). Cassava cultivated in soil contaminated with heavy metal as well as petroleum hydrocarboncontaminants will end up producing cassava tubers accumulated with heavy metals and petroleum hydrocarbon contaminants in quantities that may be harmful to humans and as such disrupt its potential end uses. The release of heavy metals such as lead, copper, chromium and other contaminants from the exploration and exploitation of oil such as benzene and the like can be absorbed into the cassava tubers thereby making the edible tuber carcinogenic as well as distorting the growth of the cassava plant in general (Kigigha et al., 2018).

Study Area

Fig 1 Sampled site: Omoku, Rivers State

Methods

The cassava (*Manihot esculenta*) samples were collected from three different farms located at Ebocha, Obrikom and Obagi. The cassava (*Manihot esculenta*) sample used as a control was collected from Aluu. The samples were collected on a dry sunny day between August 2022 and September 2022 from the three farms and were stored in different black airtight polyethylene bags and transported to the Chemistry Laboratory of Ignatius Ajuru University of Education at Rumuolumeni, Port Harcourt for laboratory analyses.

A plastic shovel was used to randomly collect soil samples from three different farms located at Ebocha, Obrikom and Obagi. The soil samples used as the control sample were collected from Aluu. The samples were collected on a dry sunny day between August 2022 and September 2022 from the three farms and were stored in different black airtight polyethylene bags and transported to the Chemistry Laboratory of Ignatius Ajuru University of Education at Rumuolumeni, Port Harcourt for laboratory analyses.

The soil samples were air dried to a constant weight for four to five days and with the useof mortar and pestle were ground to powder, then sieved with a 2mm mesh sieved and stored in a clean airtight amber bottle and labelled accordingly and stored until they were analysed.

The randomly collected cassava tubers were washed properly with tap water before peeling them. The edible cassava tubers were cut into neat slices of about $5cm³$ to improve their surface area to promote easy drying. They were separately washed properly again to eliminate contamination and then spread on four different plastic ovens labelled

appropriatelyto represent cassava samples from Ebocha, Obrikom, Obagi and control, then sun-dried to aconsistent weight for four to five days. A mortar and pestle were used to pulverize the cassava samples and store them in airtight glass bottles.

5g of the soil samples each were weighed and transferred into a digestion flask. 9ml of concentrated hydrochloric and 3ml of concentrated trioxonitrate (vi) acid on a ratio of 3:1 was added to the sample and properly agitated and then placed in the fume cupboard and heated using a heating mantle until the sample became dry. The dried samples were allowed to cool thereafter, 100ml of distilled water was measured with a volumetric flask into the driedsample and agitated. The digest was filtered with Whitman filter paper and transferred to clean 250ml sample bottles labelled appropriately. An Atomic Absorption Spectrophotometer (AAS) was then used to subject the digest to heavy metal analysis, and each soil samples were analysed for Cd, Cr, Cu, Fe, Pb and Ni.

5g of the cassava each was weighed into a digestion flask then 15 ml of diluted hydrochloric acid and 3 ml of trioxonitrate (v) acid were added and agitated, then placed in a fume cupboard and heated to dryness. They were then allowed to cool and 100ml of distilled water was added to the dry sample and agitated. The digest was filtered with Whatman filter paper andtransferred to clean 250ml sample bottles labelled appropriately. Atomic Absorption Spectrophotometer (Technology network Atomic Absorption Spectrometer Model; SN-PGAA 500) was then used to subject the digest to heavy metal analysis, and each cassava samples were analysed for Cd, Cr, Cu, Fe, Pb and Ni.

The digested samples were aspirated into a flame where they became atomized, and a light beam was directed through the flame into a monochromator and then onto a detector that measures the intensity of light absorbed. AAS is sensitive in that, it depends upon the presence of free unexcited atoms. Each metallic element has its characteristic absorption wavelength; hence a source lamp of that element was employed which takes care of spectral and radiation interferences. The amount of light intensity absorbed in the flame was proportional to the concentration of the element in the sample. The values of metal concentration were read directly from the extrapolated calibration curve in the system.

50g each of the samples were weighed and transferred into the soxlet extraction unit. 150ml of solvent ethyl acetate was measured and transferred into the extraction unit and then was heated for 1 hour. The samples were allowed to cool, then it was transferred into a sample bottle for laboratory analysis. The detection and the quantification of TPH in soilsamples were carried out using a Gas Chromatograph-Flame Ionization Detector (Agilent/ HP 6890 GC PLUS) instrument, where a 3 μl of concentrated sample eluted from column was injected into GC vial. The blank DCM was injected into a micro-syringe of GC to clean the syringe (3 times) before taking the sample for analysis. The microsyringe was rinsedwith the sample and the sample was injected into the column for quantification of the TPH sample. After separation, the compounds were passed through a flame ionization detector, as FID detects the compounds in the sample. The amount of TPH was resolvedat a particular chromatogram in mg/kg for the soil sample.

Using a mortar and pestle, each cassava (*Manihot esculenta*) sample was pulverized

to powder, thereafter 50g of each of the samples was weighed and transferred into the soxhlet extraction unit. 150 ml of solvent ethyl acetate was measured and transferred into the extraction unit and then was heated for 1 hour. 1.0 ml of the organic extract was then transferred into a vial and analysed by GC-FID (Agilent/ HP 6890 GC PLUS) in the Chemistry Laboratory, Ignatius Ajuru University of Education

The contamination factor was used to determine the levels of soil contamination by heavy metals. The ratio of the measured concentration to the natural abundance of a given metal has been proposed as the contamination factor (CF) being classified into four grades for monitoring the pollution of metals. Table 3.1: Intervals of Contamination Factor

Very high degree ($CF \ge 6$).

Contamination factor (CF) = $\frac{Cm}{Cb}$

Where Cm = concentration of measured metal

 $Cb =$ background value The background value taken is considered from the world average value in shale (mg kgG¹) of the metals determined in the study. The values are Fe = 47200, Pb = 20, Cu = 45, Cr = 90, Ni = 68, and Cd = 0.3.

(1)

Determination of pollution load index (PLI)

PLI is used to evaluate soil quality, For the entire study area, PLI was determined as the *nth* root of the product of n CFs, according to the formula:

$$
PLI = \sqrt[n]{(CF1 \times CF2 \times CF3 \times \times Cfn)}
$$
\n(2)

PLI = 0 indicates excellence, PLI = 1 suggest the presence of only a baseline level of pollutants and PLI > 1 indicates progressive deterioration of the site. The PLI evaluated the overall toxicity status of the sample. The accumulation factor (ACF) was estimated for the ability of cassava to absorb heavy metals. The accumulation factor is the ratio of the plant metal content to the soil content. The ACF is calculated using the following formula:

$$
ACF = Cplant / Cosil . \t\t(3)
$$

Where Cplant is the metal concentration in the plant and Csoil is the metal concentration in the soil

Results **Table 1: Mean levels of heavy metals in cassava samples from Omoku (Obagi, Obrikom, Ebocha) and a control point**

mg/kg LOCATIONS

Table 4: Contamination factor and PLI of heavy metals in the soil of Omoku (Obagi, Obrikom, Ebocha) and a control point

Source: Researchers field data

PLI: Pollution Load Index

Source: Researchers field data

Discussion

Heavy metals in cassava samples from Obagi, Obrikom and Ebocha

The mean values of Fe in cassava ranged between 66.032 ± 0.13 and 87.49 ± 0.07 mg/kg with an overall mean of 75.37±10.99 mg/kg. They were all above the WHO and DPR limit except the control which was found below the standard limits with mean levels of 45.19 ± 0.23 mg/kg. The highest concentration of heavy metals in all the locations was found to be Fe (87.49±0.07 mg/kg) in cassava samples from Ebocha and this may be due to discharges of untreated wastes from school laboratories and the District Hospital which are the main sources of waste into that section. Fe levels recorded in this study were high when compared to values reported by Alege, et al. (2020) and this could be due to the high emission of pollutants containing Fe in the area.

The mean values of Cu in cassava ranged between $5.86\pm0.00 - 8.54\pm0.02$ mg/kg with an overall mean of 7.19 ± 1.09 mg/kg. They were all within the WHO and DPR limits. The presence of Cu is due to discharges from residential dwellings, groundwater infiltration, and industrial discharges or the abattoir close by. The mean values of Cr in cassava ranged between $5.17\pm0.04 - 7.43\pm0.00$ mg/kg with an overall mean of 6.37 ± 1.08 mg/kg. They were all above the WHO and DPR limits except the control which was found below the standard limits with mean levels of 2.17 ± 0.00 mg/kg. The high concentration of Cr could be due to the release of untreated airborne emissions, waste products from chemical plants incineration and topsoil and rock leaching into the environment from the activities of oil and construction companies sited in the area. The mean values of Pb in cassava ranged between $1.70\pm0.00 - 3.62\pm0.00$ mg/kg with an overall mean of 2.60±1.05 mg/kg. They were all above the WHO and DPR limit which could be due to the discharge

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of contaminants containing Pb into the environment at a high concentration. Pb levels recorded in this study were high when compared to values reported by Ajayi and Olasukanmi (2021) and this could be due to the high emission of pollutants containing Pb in the area. The mean values of Ni in cassava ranged between 1.723±0.05 and 5.801±0.01 mg/kg with an overall mean of 4.38±1.38mg/kg. They were all above the WHO and DPR limits. The high concentration may be attributed to the presence of industrial wastes (discarded batteries, plastics, galvanized pipe remnants, condemned zinc materials, effluents etc) from the activities of oil and construction companies situated in the area. The mean values of Cd in cassava ranged between $0.05 \pm 0.00 - 1.41 \pm 0.00$ mg/kg with an overall mean of 0.54±0.06 mg/kg**.** Obrikom and Ebocha were found above the WHO and DPR limit while Obagi was found above the WHO limit but below DPR.

Heavy Metals in soil samples from Obagi, Obrikom and Ebocha

The mean values of Fe in soil ranged between 67.17 ± 0.00 and 87.51 ± 0.08 mg/kg with an overall mean of 76.08±10.40 mg/kg. They were all below the WHO and DPR limit except the control which was found below the standard limits with mean levels of 45.49 ± 0.07 mg/kg. The highest concentration of heavy metals in all the locations was found to be Fe (87.51±0.08 mg/kg) in the soil sample from Obagi. Fe levels recorded in this study were low when compared to values reported by Škrbić et al. (2013) and this could be due to low emission of pollutants containing Fe in the area. The mean values of Cu in soil ranged between $7.97\pm0.01-8.74\pm0.02$ mg/kg with an overall mean of 8.48±0.65 mg/kg. They were all within the WHO and DPR limits. The mean values of Cr in soil ranged between 9.38 \pm 0.00–9.63 \pm 0.05 mg/kg with an overall mean of 9.51 \pm 0.04 mg/kg. They were all within the WHO and DPR limits. Chromium levels recorded in this study were low when compared to values reported by Ogbonna et al. (2013) and this could be due to low emission of pollutants containing Cr in the area. The mean values of Pb in soil ranged between 7.65±0.00 – 8.56±0.03 mg/kg with an overall mean of 8.02±0.56mg/kg. They were all within the WHO and DPR values. Pb is a heavy metal and at a high concentration can be disastrous to humans. Human exposure to lead causes severe toxicity. Pb levels recorded in this study were high when compared to values reported by Lakić et al. (2020) and this could be due to the high emission of pollutants containing Pb in the area. The mean values of Ni in soil ranged between $7.48\pm0.07 - 8.72\pm0.05$ mg/kg with an overall mean of 7.93 ± 0.68 mg/kg. They were all within the WHO and DPR limits. Ni levels recorded in this study were high when compared to values reported by Igwegbe et al. (2013) and this could be due to the high level of pollution of lead in the environment. The mean values of Cd in soil ranged between $2.61\pm0.01-6.78\pm0.01$ mg/kg with an overall mean of 4.03 ± 2.38 mg/kg. They were all above WHO standard while Obagi and Obrikom were found below DPR limit. Cadmium is the most toxic element, even at its low concentration in the food chain. Cadmium toxicity causes renal dysfunction lung cancer, and also osteomalacia in the human population and animals.

TPH in cassava and soil samples from Obagi, Obrikom, and Ebocha

The mean levels of total petroleum hydrocarbon determined in cassava were 442.00±16.26, 320.67±0.88 and 255.33±6.39 mg/kg for Obagi, Obrikom and Ebocha respectively. In the soil, the mean levels of total petroleum hydrocarbon determined include 1095.00±3.00, 895.67±0.88 and 647.33±6.67 mg/kg for Obagi, Obrikom and Ebocha respectively. The highest concentration of total petroleum hydrocarbon in cassava was found in Obagi $(442.00\pm16.26$ mg/kg) while the lowest concentration was discovered in Ebocha (255.33±6.39 mg/kg). In the soil, the highest concentration of total petroleum hydrocarbon was found in Obagi (1095.00±3.00 mg/kg) while the lowest concentration was discovered in Ebocha (647.33 \pm 6.67 mg/kg). The presence of TPH in soil samples collected from all locations must have been the reason for its presence in cassava samples collected from these locations. One would have expected to havea higher value for soil samples from Ebocha because more oil exploration is being done there, but from observation, one can say that the high value at Obrikom and Obagi could be a resultof the waste disposal system, as Obrikom and Obagi have experienced more of oil spillages than Ebocha.

Contamination factor and PLI of heavy metals in the soil of Obagi, Obrikom and Ebocha.

The contamination factor observed in Obagi Obrikom, Ebocha and the control point for all the metals include Cr (0.10, 0.11, 0.11, and 0.03), Cd (9.00, 8.77, 22.6 and 7.2), Pb (0.38, 0.39, 0.43 and 0.084), Cu (0.19, 0.18, 0.19 and 0.02), Fe (0.0018, 0.0015, 0.0014 and 0.0009) and Ni (0.11, 0.13, 0.11 and 0.04). A very low degree of contamination was observed for Cr, Pb, Cu, and Fe in all the locations and a very high degree of contamination was observed for Cd in all the locations. The Pollution load index was also used to ascertain the levels of soil pollution by heavy metals. It was observed that the PLI values for Obagi, Obrikom, Ebocha and control are 0.15, 0.15, 0.18 and 0.05 and were all less than 1 (PLI<1) indicating that all the locations where sampling took place were unpolluted with heavy metals.

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Bioaccumulation factor of heavy metals in cassava of Obagi, Obrikom and Ebocha

The bioaccumulation factor observed in Obagi, Obrikom, Ebocha and the control point for all the metals include Cr (0.53, 0.68, 0.77, and 0.81), Cd (0.019, 0.065, 0.21 and 0.00), Pb (0.22, 0.32, 0.42 and 0.65), Cu (0.67, 0.89, 0.98 and 2.52), Fe (0.83, 0.89, 1.30 and 0.99) and Ni (0.58, 0.35, 0.76 and 0.62). The highest bioaccumulation factor of the heavy metal was Fe and the lowest was discovered to be Cd. The bioaccumulation factor of the heavy metals was observed.

Conclusion

This research investigated the concentration of some heavy metals (Cd, Cr, Cu, Fe, Pb and Ni) and total petroleum hydrocarbon in soil samples as well as cassava tubers harvested from Omoku Metropolis in Ogba-Egbema-Ndoni Local Government Area of Rivers State. In some of the analyses, the heavy metal results fell above WHO, FME and DPR recommended standards and it was discovered that a few of the parameters were above the set limit for the samples. The mean levels of the TPH were observed to be high and this is proof that the consumption of cassava from Omoku may have the ability to cause health hazards to the inhabitants in the area if consumed over a long period.

Recommendations

- i. As a result of the increase in concentrations of some heavy metals in the cassava from Omoku, emissions should be minimized.
- ii. Owing to the concentrations of some of the heavy metals in the soil samples, engagement sessions by the companies with the community can still be used to enlighten the people on the dangers of contaminated soil and the way forward to prevent soil pollution.
- iii. As a result of the concentrations of some heavy metals observed from the contamination factor and bioaccumulation factor, prevention measures should be carried out
- iv. The government should implement policies to curb anthropogenic activities capable of contaminating the environment by making a huge sum of money compulsory as payment by companies per discharge.
- v. Due to the high concentration of TPH in the samples from Omoku, companies should be made to recycle their byproducts.

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