

# REMEDICATION OF HEAVY METALS CONTAMINATED SOILS IN PORT HARCOURT ENVIRONMENT

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**Abstract:** This study aim to evaluate the remediation of heavy metals contaminated soils in Port Harcourt environment. Four samples from four locations within the foreshore were investigated for four months. The findings from the parameters analysed show SEM values of pH as  $7.60\pm 0.10$ , Temperature  $30.25\pm 0.25$ , Total hydrocarbon content  $47.08\pm 6.71$ , Zinc  $6.82\pm 0.51$ , Lead  $0.35\pm 0.06$ , Cadmium  $0.0025\pm 0.0009$ , Copper  $0.08\pm 0.01$ , Nickel  $0.05\pm 0.01$ mg/kg, respectively in diesel contaminated soils when compared with the SEM values of control. The effect of contaminated and treated soils on heavy metals reveal that soils contaminated with diesel (P1) and spent oil (P2) show increase in SEM values when compared with control. However, there was a decrease in the concentration of heavy metals when soils polluted with Diesel were treated with  $\text{NaNO}_3 + \text{K}_3\text{PO}_4$  (T1), and with  $\text{NH}_4\text{NO}_3 + \text{K}_3\text{PO}_4$  (T2), respectively. Similarly, soils polluted with spent oil and treated with  $\text{NaNO}_3 + \text{K}_3\text{PO}_4$  (T3), and the others treated with  $\text{NH}_4\text{NO}_3 + \text{K}_3\text{PO}_4$  (T4) also showed a decrease in the concentration of heavy metals, respectively. It was therefore concluded that impact of heavy metals on soils aggravated by oil spills was remediated by the application of sodium nitrate/Potassium phosphate or Ammonium nitrate/Potassium phosphate, thus establishing the fact that these chemicals can serve as a good option in any remediation process of the soil. However, Ten Percent Sodium nitrate/One Percent Potassium phosphate ( $10\% \text{NaNO}_3 + 1\% \text{K}_3\text{PO}_4$ ) remediated better than Ten Percent Ammonium nitrate/One Percent Potassium phosphate ( $10\% \text{NH}_4\text{NO}_3 + 1\% \text{K}_3\text{PO}_4$ ) and was more economical for the remediation of heavy metals.

**Keywords:** Heavy Metals, Remediation, Contaminated, Soils.

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## 1. INTRODUCTION

The Soil is known to be the unattached organic mineral material found on the surface of the earth which is subjected to different environmental impacts ranging from weather and climatic conditions, presence of micro and macro-organisms, water level, temperature variation, and the cyclic movement of decomposition. Their primary functions include; supporting the growth of plants and trees, staying as a habitat for micro and macro organisms, capacity to control the water transport in hydrologic systems. It can also be a medium for engineering activities and a vital factor in the recycling structure of Nature. Soil pollutants are of different forms and are likely heavy metals from fuel spillage. Most times they could include hydrocarbons, pesticides, etc, but in whichever case, they are detrimental to the environment especially on soils meant for planting, which if used, without undergoing remedial options inflicts several health challenges on humans as a result of eaten-agricultural products from the contaminated soil. Health Challenges as a result of these contaminant vary according to immunities but they are majorly tumorigenesis and mutagenesis. The Aim of this study is to evaluate the remediation of

heavy metals contaminated soils in Port Harcourt environment. The Chemistry of heavy metals has been a contributory factor to food chemical components. In their less toxic levels, they become useful as they take up the roles of maintaining the sustainability and equilibrium levels of the ecological environment. Liu, *et al.* (2010) described Iron is one of the most substantial metals, proven to easily mix with oxygen, and form a compound adequate for vital purposes. Meanwhile, Bae *et al.* (2010) in their research illustrated the significant functions that Zinc plays in dermatology. Copper can be used as a treatment for fish diseases and to cure sicknesses of radiation. Nagajyoti *et al.* (2010) contended that in trace amounts, most of the heavy metals are of importance to plant metabolism. The adverse effect of heavy metals are potential threats to our health since products from the soil are the major foods we eat. This leads to remediating the soil that ignored the discovery of so many techniques. However, for these techniques of immobilization and stabilization to be achieved, some soil amendments are required to revitalize, remediate and recycle the soil.

## 2. MATERIALS AND METHODS

The study area are the soils of Port Harcourt Local Government Area of Rivers State. Composite samples were made from these and the distribution of physical and chemical speciation of their heavy metal contents analysed. Four undisturbed soil samples were collected from four different locations Viz: Mile one, Eastern by Pass, Tere-Ama and Bundu waterside. Surface soil samples (0-30cm) from Mile one, Eastern by Pass, Tere-ama burro pit and Bundu waterside were collected using soil Auger. The sampling points were randomly chosen. For each point, samples were collected at a depth of 0 – 30cm respectively giving a total of four samples.

### Soil Treatment:

2kg of soil samples was collected from each of the four locations. The samples were air-dried and sieved using 2mm sieve mesh. Some quantity of the soil samples was collected and analyzed first for Heavy metals and physicochemical properties using standard methods described below. Secondly, 555g of each of the soil samples was weighed into plastic buckets: Each bucket containing the soil sample was poisoned with 20ml of Diesel and the other contaminated with 20ml of spent oil for the four locations. The buckets were kept for one month in the corridor for proper mixing and aeration, after which, the contaminated samples from the buckets were taken to the laboratory for analysis. Thirdly, the other contaminated samples were fertilized differently for four months with 10:1 ratio of  $\text{NaNO}_3 + \text{K}_3\text{PO}_4$ , and  $\text{NH}_4\text{NO}_3 + \text{K}_3\text{PO}_4$  respectively (for the buckets of soil containing diesel and to the other buckets containing spent oil). The soil were then analyzed to note the level of remediation by these chemical methods.

### Determination of pH and Temperature.

Measurement of pH by electrometric method using Electronic pH Meter (ASTM, 1999) is done to determine the acidity or alkalinity of the sample.

### Procedure:

The pH level of the samples was determined with the use of a portable pH meter (model DSPH-1BUS). The meter was calibrated prior to use with buffer solutions of pH 7, 4 and 10 of known calibration standard, after which the electrodes were thoroughly dipped in distilled water. 10g of each of the soil samples was weighed out after sieved using a 2mm sieve mesh into a 250 ml beaker, 25 ml of distilled water was added and allowed to stand for 30 minutes and stirred occasionally with a glass rod. The instrument was powered on and the reading allowed to stabilize. Upon meter stabilization, the reading on the meter was recorded as the pH of the samples. The probe was rinsed in distilled water, and the display mode adjusted after each measurement. The electronic meter is capable of reading temperature and it was immediately switched to the temperature mode after each pH measurement. The stable reading on the screen was recorded as the temperature of the samples.

### Determination of heavy metals

**Soil pre-treatment:** 5g of air dried soil samples was weighed out after sieved into a 100ml flask using a 2mm sieve mesh, 2ml of  $\text{HNO}_{3(\text{aq})}$  and 6ml of  $\text{HCl}_{(\text{aq})}$  was added in the ratio of 1:3 to the already weighed sample. The mixture was digested by heating on a heating mantle until the sample attained near dryness to enable proper leaching of the sample. The sample was then diluted with distilled water and filtered using the watchman No. 42, 150mm diameter filter paper into a 50ml volumetric flask. The filtrate was then made up to 50ml mark. The atomic absorption spectrometer (AAS) was calibrated

using a standard solution for each of the metals of interest. The digested sample is then introduced into the AAS and the concentration of the metals were displayed.

#### Determination of Total Hydrocarbon Content (THC)

Residual Total Hydrocarbon Contents (THC) were extracted from the samples and quantified using UV- spectrophotometer.

**Extraction:** 2g each of the soil samples was weighed into a clean extraction amber container. 10 ml of extraction solvent (pentane) was added into the sample and mixed thoroughly and allowed to settle. The mixture was carefully filtered into clean solvent rinsed extraction bottles using filter paper fitted into Buchner funnels. The extracts were concentrated to 2 mL and then transferred for separation.

**Separation:** The total hydrocarbon content was carried out following ASTM (1999) Soxhlet Extraction Method using Hexane Extractable Materials by American Society for Testing and Materials). 10g of each of the soil samples was weighed into a 250 ml conical flask and 20 ml of Xylene was added and then placed on a reciprocating shaker for 30 minutes. The soil solution was later filtered using No. 1 Whatman 11 cm filter paper. The concentration of each soil sample was determined using a 21D spectrophotometer (CECIL 3041) at a wavelength of 650 nm. A set of standards: 0.00, 5.00, 10.00, 15.00, 20.00 and 25.00 ppm was prepared and read on the spectrophotometer to calibrate the equipment before the final result was calculated. However, 0.5 g of each of the oven-dried sample was used for the determination of THC in the samples using the same procedure.

#### Statistical analysis

Data was presented as Mean  $\pm$ SEM (Standard error of mean). A statistical comparison of means of different treatments was carried out using one-way analysis of variance (ANOVA) followed by *Dunnnett's* post-hoc test, and treatment means were separated using the Duncan Multiple Range Test. Significance level was considered at  $p < 0.05$ . Data was analyzed using Graph Pad prism 6.0 statistical software.

### 3. RESULTS AND DISCUSSION

Physicochemical parameters of soils under investigation was accessed to determine the effects of treatments on the soil properties. A comparative study of the pH values of the control and that of the diesel contaminated soils reveal an increase in the pH value ( $7.60 \pm 0.10$ ) when compared to the normal. Significant increase in pH value at  $p < 0.05$  was seen in diesel contaminated soils remediated with  $\text{NaNO}_3 + \text{K}_3\text{PO}_4$  at mean values ( $11.13 \pm 0.26$ ). Also, at  $p < 0.05$ , the pH values of diesel contaminated soils treated with Ammonium nitrate and Potassium phosphate was recorded as  $10.45 \pm 0.31$  when compared to the pH of the untreated soil, with mean value of  $7.50 \pm 0.04$ . Similarly, at  $p < 0.05$ , increase in the values of pH was observed in spent oil polluted soil treated with Sodium nitrate/Potassium phosphate and Ammonium nitrate/Potassium phosphate, respectively. This findings indicate that treatment with the chemicals under study raised the pH value towards alkalinity. Changes in the pH values greatly affects the nature of the soil. Soils with very low pH values indicates acidity which may give rise to soluble magnesium and aluminum which is toxic to plants. Soils with high pH affect the availability of nutrients in the soil. The increase in the pH of the soil may be due to the hydrophobic nature of the diesel which could induce salinization. The findings of this study are in consonance with Wang *et al.*, 2010 who posited that crude oil contaminated sites experience increase in pH values.

The results of the soil temperature reveal a slight increase in the value of the temperature of diesel contaminated soil and spent oil contaminated soil at values  $30.25 \pm 0.25$  and  $30.38 \pm 0.13^\circ\text{C}$ , respectively. More, during microbial activities, big and complexes of molecules are broken down accompanied the liberation of energy; some are used up while the remaining are released in form of heat. This effect may be attributed to the action of hydrocarbon degrading micro-organism inducing high temperature or the heat content of the diesel and the spent oil which may aggravate microbial activity. It is well established that the action of microorganisms on hydrocarbon is accompanied by the release of heat synonymous to rise in temperature. However, the reduction in these values were seen when Diesel contaminated soil was treated with sodium nitrate/ Potassium phosphate while spent oil contaminated soil also showed significant reduction in the temperature. The implication of this result is that the chemical under study can be used to reduce the impact of the degradation caused by the pollutant under investigation. The temperature increase in the polluted soils could be as a result of the reaction kinetics of Diesel and spent oil.

Total Hydrocarbon content has higher values in soils contaminated with diesel oil and spent oil, with values of  $47.08 \pm 6.71$  and  $56.72 \pm 8.29$  mg/kg when compared to the control ( $23.55 \pm 5.36$  mg/kg) at  $p < 0.05$ . These values were seen to have increased significantly when contaminated soils were remediated with certain chemicals. Comparing T1 and T2 to P1, the concentration values decreased at  $p < 0.05$ . However, a more significant decrease was seen in T1. T3 and T4 which showed significant decrease in Total hydrocarbon content when compared to soil contaminated with spent oil.

Heavy metals constitute an ill-defined group of toxic metals. These metals have been extensively studied and their effects on the environment regularly reviewed by international bodies such as the World Health Organization (WHO) 2011. The effect of contamination of soils by Diesel and Spent oil and its remediation by some chemical treatment on heavy metals concentration in soils have been assessed for its pollution status.

The results of zinc showed increase in the concentration of zinc metal in diesel contaminated soil with mean value of  $6.82 \pm 0.51$  mg/kg when compared to the normal. The impact of the contamination was remediated at T1 ( $4.79 \pm 0.07$  mg/kg) and T2 ( $4.39 \pm 0.11$  mg/kg) at 95% confidence level.

Lead (Pb) concentration increased from control ( $0.25 \pm 0.02$  mg/kg) to P1 ( $0.35 \pm 0.06$  mg/kg), but decreased when treated with T1 and T2. On the other way, the contaminated soil (P2) showed very low values of Pb when compared with the treated soils (T3 and T4). However, when contaminated soils were compared with the treated soils, there was a significant reduction level at 95% ( $P < 0.05$ ) confidence limit in T1 ( $0.15 \pm 0.02^a$ ) and T4 ( $0.18 \pm 0.03^a$ ), respectively.

Cadmium (Cd) levels increased when the soils were remediated with all the treatments. However, when the contaminated soils (P1 and P2) were compared with the remediated soils, there was 95% ( $P < 0.05$ ) significant reduction at T3 ( $0.021 \pm 0.005^c$ ) and T4 ( $0.0075 \pm 0.0005^c$ ) respectively.

The concentration of Copper (Cu) (mg/kg) was lowered when the soils were contaminated with both diesel and spent oil. The same trend occurs in the remediated soils compared with the control. When the contaminated soils were compared with the control, there was a significant difference with the control ( $0.14 \pm 0.07^*$ ) at  $P < 0.05$  confidence interval.

There was also a significant reduction at 95% ( $P < 0.05$ ) confidence interval when the contaminated soils were compared with remediated soils, with T2 recorded as  $0.44 \pm 0.001^a$ . The mean Ni content decreased when contaminated with Diesel, but increased tremendously when the soils were contaminated with spent oil. However, when Ni contents of the contaminated soils were compared with the treatments, there was a significant reduction in T1 ( $0.17 \pm 0.02^c$ ) and T3 ( $0.07 \pm 0.007^a$ ) at  $P < 0.05$  confidence limits, respectively.

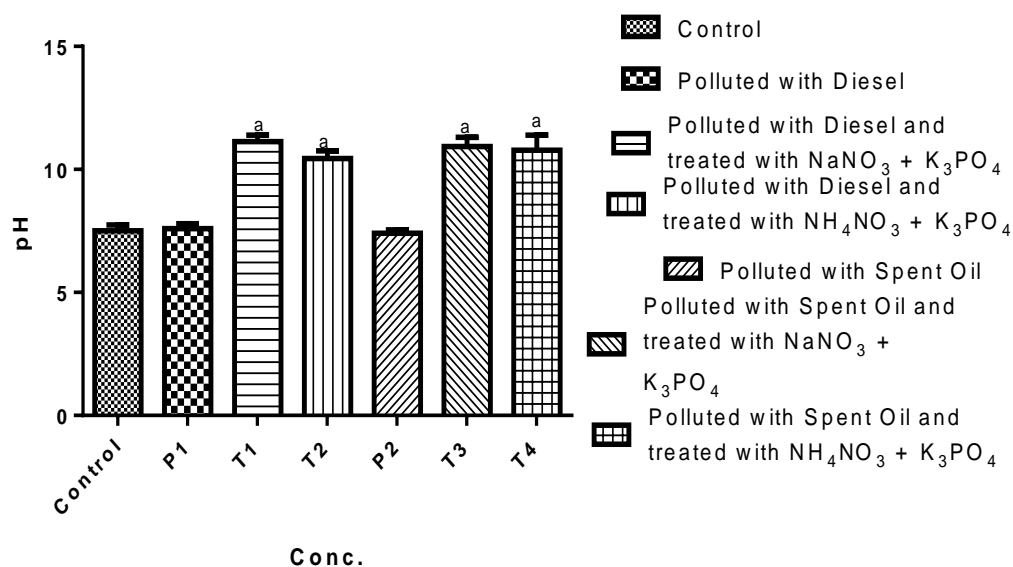


Fig.1: pH of contaminated and remediated soils from the study area.

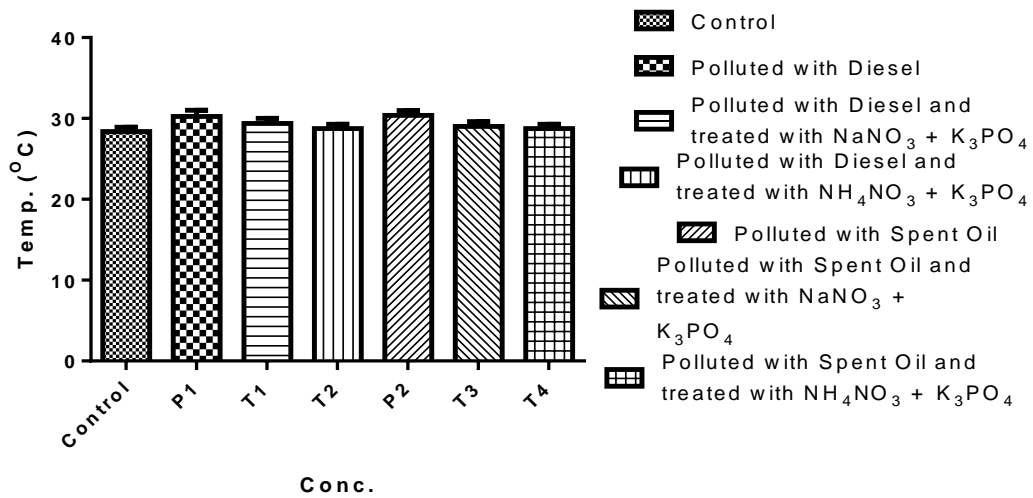


Fig.2: Temp. (°C) of contaminated and remediated soils from the study area

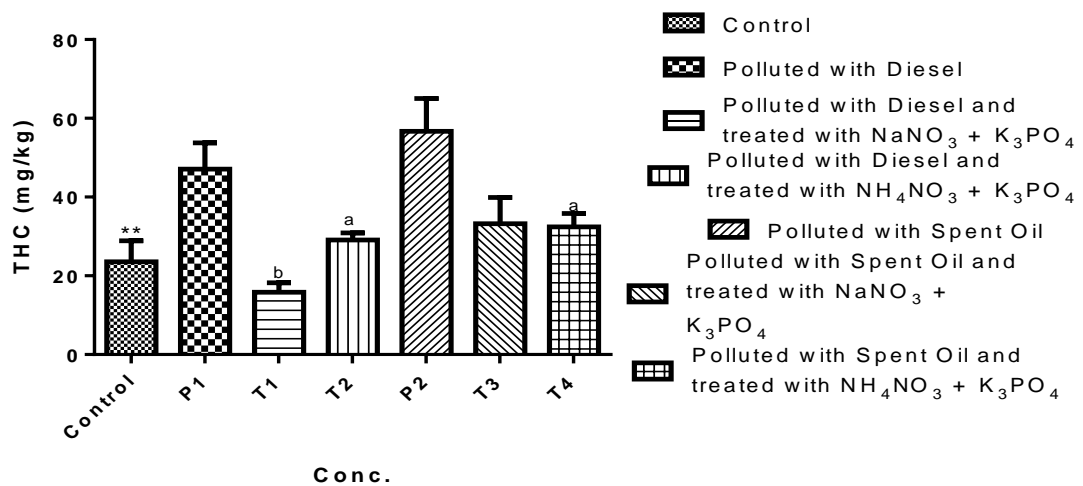


Fig.3: THC (mg/kg) of contaminated and remediated soils from the study area

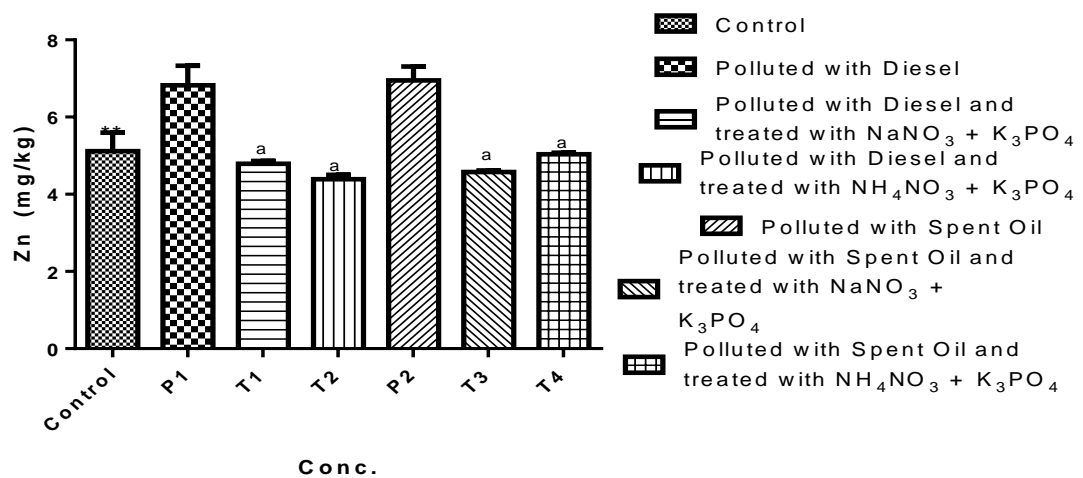


Fig.4: Zn (mg/kg) of contaminated and remediated soils from the study area

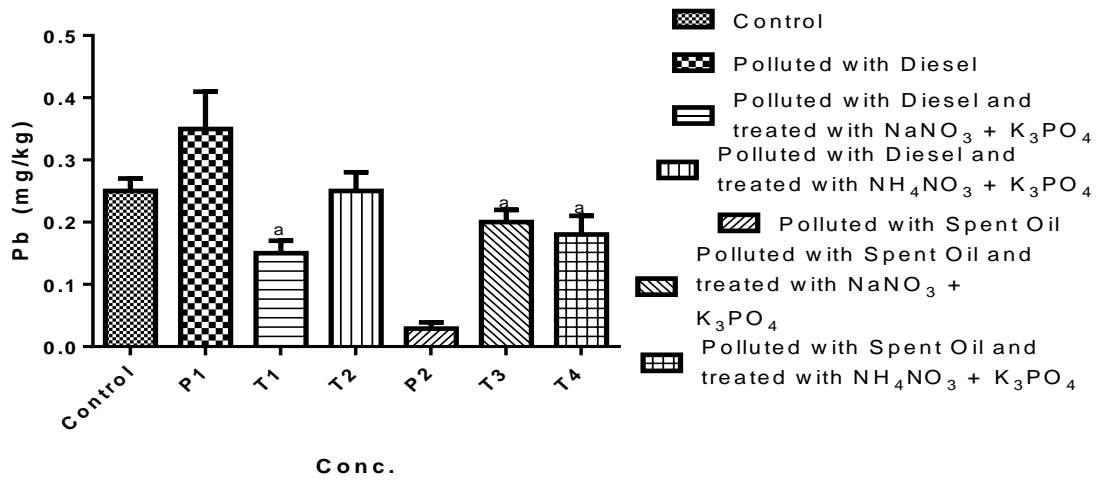


Fig.5: Pb (mg/kg) of contaminated and remediated soils from the study area.

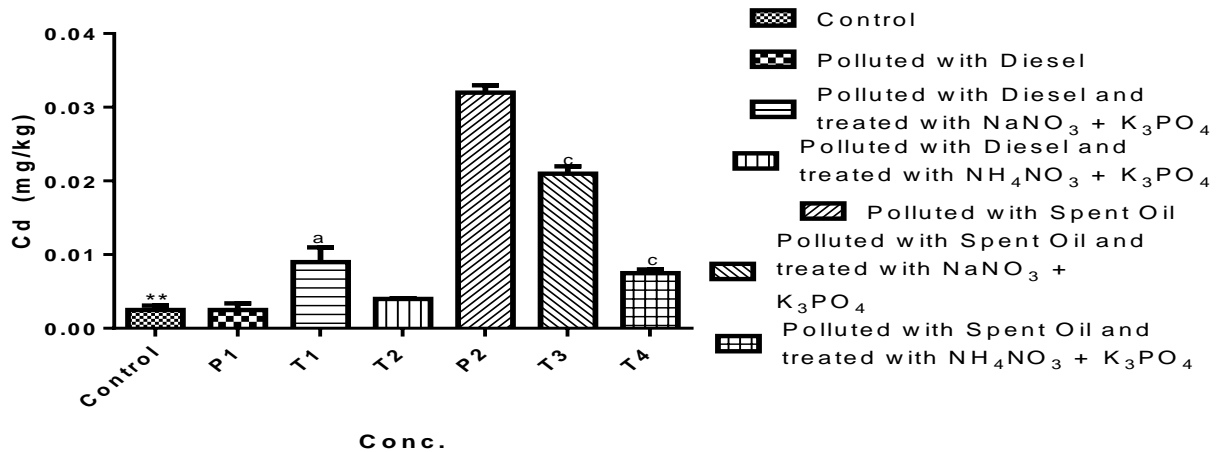


Fig.6: Cd (mg/kg) of contaminated and remediated soils from the study area.

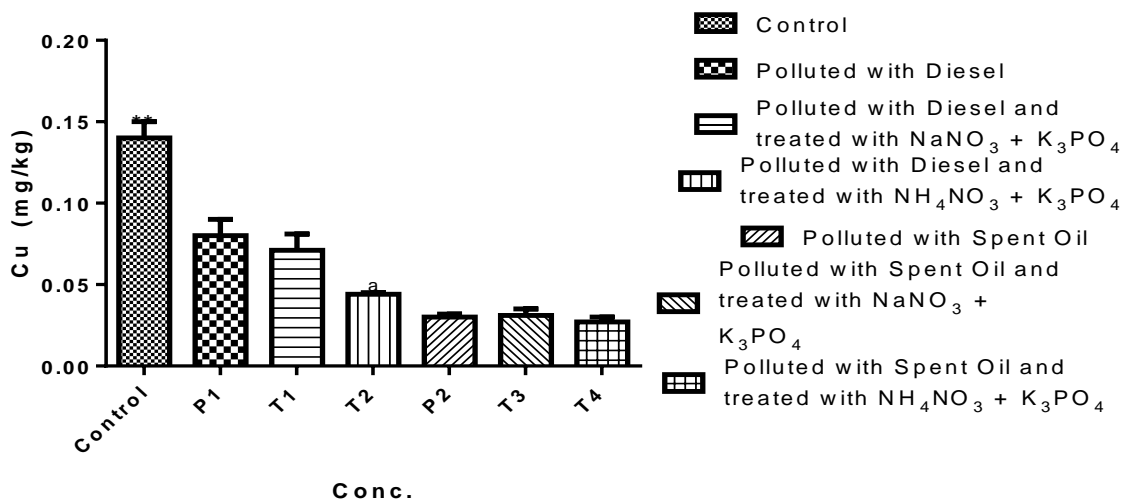


Fig.7: Cu (mg/kg) of contaminated and remediated soils from the study area



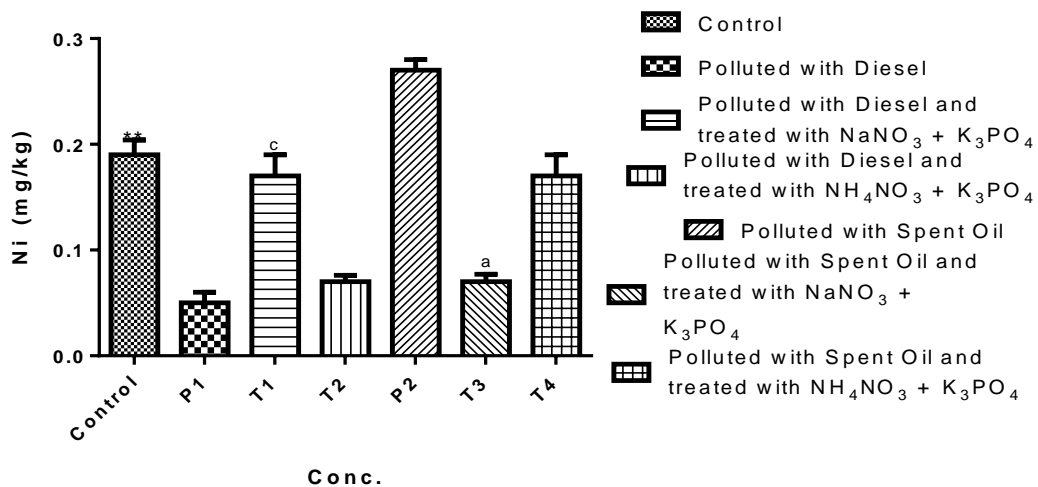


Fig.8: Ni (mg/kg) of contaminated and remediated soils from the study area

#### 4. CONCLUSION

Finding the best approach towards remediation of soil contaminated with crude oil fraction and the removal of hydrocarbon pollutant from the environment has been a critical issue for the past decade. Researchers have subjected various assertions to experimentation to determine the best and cost-effective method of total restoration to normalcy of soils contaminated with crude oil fraction. This study sought to validate the remediation of heavy metals contaminated soils in Port Harcourt environment. Careful observations and the analysis of contaminated and uncontaminated soils provided insight on the level of heavy metals concentration soils. Diesel and spent oil were used to contaminated soil samples and the results obtained showed that the soils were affected, heavy metals in the soils were analyzed and observations made show that oil spills aggravated the presence of heavy metals. However positive remediation was observed in soils with elevated heavy metals when treated with Sodium Nitrate/ Potassium phosphate and Ammonium nitrate/ Potassium phosphate.

The study therefore concluded that impact of heavy metals on soils aggravated by oil spills were remediated by the application of Sodium nitrate / Potassium phosphate and Ammonium nitrate/Potassium phosphate, respectively. Thus, establishing the fact that these chemicals can serve as a good option in any remediation process of the soil. However, ten (10) percent Sodium nitrate / one (1) Percent Potassium phosphate remediated better than ten (10) percent Ammonium nitrate/ one (1) percent Potassium phosphate and it is more economical for remediation of heavy metals.

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