

EVALUATION OF REMEDIATION TECHNIQUES OF SOILS AFFECTED BY FUEL SPILLS IN PORT HARCOURT ENVIRONMENT

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Abstract: This study aim to evaluate the remediation of Physicochemical Properties of Soils Affected by Fuel Spills in Port Harcourt Environment. Four samples from four locations within Port Harcourt environment were investigated for four months. The findings show an increase in SEM values of Temperature ($30.25 \pm 0.25^\circ\text{C}$), Electrical conductivity ($0.97 \pm 0.11 \mu\text{S/cm}$), Sulphate ($18.73 \pm 1.92 \text{mg/kg}$), Total Organic Carbon ($0.15 \pm 0.001\%$), Total organic matter ($0.26 \pm 0.01\%$), Total hydrocarbon content ($47.08 \pm 6.71 \text{mg/kg}$) and a decrease in pH (7.60 ± 0.10) in diesel contaminated soils when compared with the SEM values of control. Alternately, the concentration of phosphate and nitrate in both diesel and spent oil contaminated soils reduced when compared with the control indicating a short fall in dissolved nutrients due to microbial activities. Positive remediation was seen in all the treatments used. However, a remediation mixture of 10% Sodium nitrate and 1% Potassium phosphate ($10\% \text{NaNO}_3 + 1\% \text{K}_3\text{PO}_4$) remediated better and faster than when 10% Ammonium nitrate and 1% Potassium phosphate ($10\% \text{NH}_4\text{NO}_3 + 1\% \text{K}_3\text{PO}_4$) was used, and was more economical. Thus, establishing the fact that these chemicals can serve as a good option in any remediation process of the soil.

Keywords: Physicochemical, Remediation, Fuel spill, Soils, Environment.

1. INTRODUCTION

Agricultural products cultivated on contaminated soils like the mechanic workshops where fuel is constantly spilled due to engine repairs were highly contaminated with physicochemical properties, especially cassava and plantain (2 majorly grown and consumed foods in the Port Harcourt Environment), thereby endangering the life of animals and humans that consume them to health risks. This is because of their bioaccumulation, non-degradability, and the excessive amounts in which they exist (Imasuen and Omorogizeva, 2013). Agriculture has been the oldest form of survival in the state. It ranges from crops cultivation, poultry farming, fish farming, and to fishing. Port Harcourt is known for producing big healthy fishes because of the surrounding aquatic environment. Furthermore, agricultural produce that can't be cultivated in the environment due to climatic conditions is imported from other states. Okereke et al. 2007 defined fuel spillage as the discharge of fuel and its products into the environment yielding from human activities. This has been announced as hazardous pollution and is still an issue to so many countries around the globe. These spills usually are made into the waters, but the ones drenched by the soil although not always noticeable are even more harmful. The best solution for fuel

spills will be to stop the flow of fuel, but Port Harcourt as a city may not survive a month without this essential commodity. This portrays how useful these resources are and how they effectuate daily activities for survival, most importantly, because it is an energy generator. 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. Hence, there must be alternative measures to curb this outflow. This leads to remediating the soil that ignored the discovery of so many techniques. The Aim of this work is to evaluate the best remediation technique of Soils Affected by Fuel Spills in Port Harcourt Environment using nutrients mixture technique.

2. MATERIALS AND METHODS

The study area are the soils of Port Harcourt Local Government Area of Rivers State. Four undisturbed soil samples were collected from four different locations, viz: Mile one, Eastern by Pass, Tere-Ama and Bundu waterside. Surface soil samples from these locations were collected using soil Auger. The sampling points were randomly chosen and were composited to make a representative sample. For each point, samples were collected each at a depth of 0 – 30cm respectively giving a total of four samples.

Soil Treatment:

About 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 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 poisoned 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 contaminated samples were fertilized differently for four months with 10% NaNO_3 + 1% K_3PO_4 and the other with 10% NH_4NO_3 + 1% K_3PO_4 in the buckets of soil containing diesel and to the other buckets containing spent oil, respectively. The soils were then analyzed to note the level of remediation by these chemical methods.

Determination of Physicochemical Parameters of Samples.

pH and Temperature

Measurement of pH was done by Electrometric Method Using Electronic pH Meter (ASTM, 1999) to determine the acidity or alkalinity of the sample. The pH 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 sieving with 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 read and 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.

Electrical Conductivity

Measurement of EC was done by Electrometric Method Using Electronic EC Meter (APHA, 1998). Soil samples were measured with the use of a Conductivity meter. The meter was calibrated prior to use with distilled water and a set of calibration standards according to manufacturer's specifications. The sample beaker was rinsed thoroughly with distilled water followed by small volume of the test sample. Some quantity of the sample was then poured into the beaker and the probe of the meter was dipped into the sample. EC reading on the screen of the meter was allowed to stabilize and values were recorded in micro Siemens per centimeters ($\mu\text{S}/\text{cm}$).

Determination of Nitrate

Ultraviolet Spectrophotometer screening method (APHA, 1998)

Procedure:

A 50ml filtered sample of each of the soil samples was taken and a 1ml HCl solution was added and mixed thoroughly.

Nitrate calibration standards were prepared in the range of 0 to 7mg NO₃⁻ N/L by diluting to 50ml. The following volumes of standard nitrate solutions 0, 1.00, 2.00, 4.00, 7.00, 35.00ml were treated in the same manner as the sample. The absorbance or transmittance was read against redistilled water set at zero absorbance (100% transmittance). The analysis was read at a wavelength of 220nm to obtain NO₃⁻ reading and a wavelength of 275nm to determine interference due to dissolved organic matter.

Calculation

Absorbance values for samples and standards were obtained by subtracting 2 times the absorbance reading at 275nm from the reading at 220nm to obtain absorbance due to NO₃⁻. A standard curve was constructed by plotting absorbance against concentration of standards. Sample concentrations were obtained correctly using sample absorbance directly from standard curve.

Determination of Sulphate

5g of air-dried soil samples was weighed out into a 250ml flask after sieving with a 2mm sieve mesh and 25ml of extracting solution (KH₂PO₄ containing 500ppm P) was added. The mixture was shaken for 30 minutes on a mechanical shaker and centrifuged. The SO₄ content was determined by turbidity.

Determination of Phosphorous

Apparatus: centrifuge, mechanical shaker, 20 ml test tube, B and L spectronic –electrophotometer.

Extracting solution- 15 mL of 1.0 N NH₄F and 25 ml of 0.5 N HCl was added to 460 ml distilled water, Stannous chloride (SnCl₂. 2H₂O) stock solution- 10g of SnCl₂. 2H₂O was dissolved in 25 ml of conc. HCl, Ammonium molybdate (NH₄)₆Mo₇O₂₄.4H₂O- 15g of ammonium molybdate is dissolved in 350 mL of 10 N HCl in a litre volumetric flask and cooled to room temperature then made up to 1 L with distilled water. 1 ml of stock solution of stannous chloride was mixed with 333 ml of distilled water. 1 g of air dried soil samples which was sieved with a 2mm sieve mesh was weighed into a 15 ml centrifuge tube and 7 mL of extracting solution was added. The mixture was shaken using a mechanical shaker and centrifuged at 2000 rpm for 15 minutes. 2 ml of the clear supernatant was pipetted into a test tube. 5 mL of distilled water was added to (NH₄)₆Mo₇O₂₄.4H₂O solution and mixed. 1 ml of SnCl₂. 2H₂O dilute solution was added and mixed. After 5 minutes, the transmittance was measured on the electrophotometer at 660 mμ wavelength.

Total Organic Carbon of Samples

Organic carbon was determined by wet oxidation method of walkley and Black [1934]. 1g of finely ground sample of each of the soil samples was weighed into a flask. 10ml of 0.1M potassium Dichromate solution was pipetted into each flask and swirled gently to wet the soil sample completely. This was followed by the addition of 20ml of concentrated H₂SO₄ using a graduated cylinder taking a few seconds only in the operation. The flask was swirled gently until soil and reagents were mixed, then vigorously for 1 minute to effect more complete oxidation and allowed to stand for 30 minutes. The contents were diluted with water to about 250ml. 25ml of 0.25M Ferrous Ammonium sulphate was then added and titrated with 0.08M potassium permanganate under strong light. The organic carbon content of the samples was calculated as the change in concentration of Ferrous Ammonium sulphate using:

$V_s \cdot M_{FAS} = V_{pp} \cdot M_{pp}$, where V_s = volume of solution; M_{FAS} = Change in concentration of Ferrous Ammonium Sulphate; V_{pp} = Volume of KMnO₄ used and M_{pp} = Morality of KMnO₄.

Total Organic Matter of Samples

Organic matter values for the samples were obtained by multiplying the organic carbon values with factors 1.724.

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

The results we obtain from this study may serve as a guiding principle for remediation or possible trigger for further research on improving on the findings of this research.

The chemical parameters of soils under investigation was assessed 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 ± 0.10) when compared to the control. 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 value of 11.13 ± 0.26 . Also, at $p < 0.05$, the pH values of diesel contaminated soils remediated with Ammonium nitrate and Potassium phosphate was recorded as 10.45 ± 0.31 when compared to the pH of the untreated soil with mean value of 7.50 ± 0.04 . Similarly, at $p < 0.05$, increase in the values of pH was observed in spent oil polluted soils remediated with Sodium Nitrate: Potassium Phosphate and Ammonium nitrate: Potassium phosphate, respectively. This findings indicate that treatment with the chemicals under study raised the pH values tending to 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 micronutrients 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. Also, crude oil elevating the soil pH could lead to rise in negative impacts attributable to alkaliscence.

The temperature of the soils were analyzed and the results reveal a slight increase in the values of temperature of diesel contaminated soils and spent oil contaminated soils at values of $30.25 \pm 0.25^\circ\text{C}$ and $30.38 \pm 0.13^\circ\text{C}$ respectively. During microbial activities, big and complexes of molecules which 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 soils were 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 chemicals under study can be used to reduce the impacts of the degradation caused by the reaction kinetics of Diesel and spent oil.

Electrical conductivity involves the measure of the amount or concentrations of ions present in the soil. Examining the electrical conductivity values of the soil samples, reveals that soils polluted with diesel showed very high significant decrease in electrical conductivity value of $0.97 \pm 0.11 \mu\text{S/cm}$ in comparison to the control site with value of $1.68 \pm 0.32 \mu\text{S/cm}$ at $p < 0.05$ (95% confidence level). This finding is in line with Osuji & Nwoye *et al.* (2007) that soils contaminated with hydrocarbon show reduction in the concentration of ions. Although, hydrocarbon do not conduct electricity but anoxic biodegradation which involves the uptake of mineral for its reaction kinetics could reduce the concentration of ions in contaminated soils thus lowering the values of electrical conductivity. However, a slight deviation was observed in soils contaminated with spent oil with an increase in value ($1.69 \pm 0.23 \mu\text{S/cm}$) when compared to the control. T1 ($1.02 \pm 0.02 \mu\text{S/cm}$) and T2 ($1.00 \pm 0.01 \mu\text{S/cm}$) which are treated contaminated soils showed significant increase

when compared to P1 ($0.97 \pm 0.11 \mu\text{S/cm}$). However, T3 ($1.17 \pm 0.17 \mu\text{S/cm}$) and T4 ($1.05 \pm 0.05 \mu\text{S/cm}$) showed a significant decrease at $p < 0.05$ when compared to P2 ($1.69 \pm 0.23 \mu\text{S/cm}$) at 95% confidence reduction interval.

Phosphorus is considered too involved in plant respiration, photosynthesis, energy storage and many other processes in plants. This makes phosphorus an important soil nutrient. Phosphorus plays a vital role in virtually every plant process that involves energy transfer. High-energy phosphate, held as a part of the chemical structures of adenosine diphosphate (ADP) and ATP, is the source of energy that drives the multitude of chemical reactions within the plant. When ADP and ATP transfer the high-energy phosphate to other molecules (termed phosphorylation), the stage is set for many essential processes to occur. There was reduction in phosphate values from 0.093 ± 0.002 in control to 0.063 ± 0.009 (mg/kg) in soils contaminated with diesel oil and 0.091 ± 0.004 mg/kg in soils contaminated with spent oil. This result is in contrast with the findings by Wyszowski *et al.* (2004) that increasing levels of soil contamination with diesel oil in series increased the phosphate content of the soil. While diesel contaminated T1 and T2 showed significant increase, a result similar to that of T3 (0.28 ± 0.005 mg/kg) and T4 (1.01 ± 0.06 mg/kg) was observed. T4 produced the highest value of phosphate (1.01 ± 0.06 mg/kg). Dissolved nutrients in the soil play a great role in the growth of plants. The contamination of soil could lead to reduction in phosphate level. Comparing the impact of the P1 and P2 to the remediation process, our findings reveal that at $p < 0.05$, an increase in phosphate value was seen indicating that the remediation process was achieved. Spent oil contaminated soil treated with ammonium nitrate and potassium phosphate showed higher level of phosphate indicating that remediation process was achieved.

Analyzing the impact of diesel contamination on the concentration of sulphate in the soil samples, results reveal a significant increase in P1 (10.24 ± 0.35 mg/kg) and P2 (18.38 ± 2.01 mg/kg) when compared to the control soil at $p < 0.05$. Comparison of T1 and T2 with P1 shows a fall or significant decrease in the values indicating that remediation is achieved at 95% confidence level ($P < 0.05$). The same observation was seen in the remediation of soils contaminated with spent oil (T3 and T4). Although the concentration of sulphate in T3 and T4 was much higher.

Nitrate nitrogen reveals the amount of Nitrogen available in the soil that are available to plants for consumption. Mineralization of soil organic matter is governed by certain factors including microbial actions. Nitrate concentration in the soil is a good indicator of available nitrogen to plants. A proper assessment of Nitrate in crude contaminated soil could reveal the extent to which damage is done to the soil. The level of Nitrate decreased in soils contaminated with diesel (P1) to 7.03 ± 2.41 mg/kg and also with spent oil (P2) to 2.11 ± 0.90 mg/kg when compared to the nitrate value of the control. A correlation of observation is seen in Onuh *et al.* (2008) that a decrease in nitrogen availability will increase levels of crude oil pollution. The indication of this result is that the concentration level of nitrate decreased in soil samples contaminated with diesel oil and spent oil and the impact of this contamination was reduced by treatment of Sodium nitrate: potassium phosphate and ammonium nitrate: potassium phosphate, respectively. It can also be inferred that the decrease in the content of nitrate is facilitated by the degradation of oil by microorganisms.

The percentage value of total organic carbon (TOC) increased significantly in samples contaminated with P1 and P2 respectively. Significance difference was observed in the values of P2 ($p < 0.05$) in comparison to the control ($0.071 \pm 0.002\%$). Organic matter content should normally increase following the addition of such levels of carbonaceous substances, but results obtained herein show that there is rather a reduction in organic carbon and organic matter contents of the contaminated soils. The most plausible connection perhaps might be that the spilled-oil impaired the metabolic processes that would have facilitated the agronomic addition of organic carbon from the petroleum hydrocarbons by reducing the carbon-mineralizing capacity of the micro flora. It is also possible that the micro-organisms present in the spilled site could not cope with the degradation of the carbon content of the diesel and spent oil. T2 showed a significant increase in the values of TOC ($p < 0.05$) when compared to P1. T4 showed a slight decrease when compared to P2. This is in contrast to T4 with slight increase when compared to P2.

Analysis of total organic matter (TOM) in soil samples contaminated with diesel and spent oil showed significant increase in values of P1 ($0.26 \pm 0.01\%$) and P2 ($0.25 \pm 0.02\%$) when compared to the control soil ($0.12 \pm 0.03\%$). Slight or no difference was seen in T1 and T3 values when compared to P1 and P2 indicating poor remediation capacity. However, the values of T2 and T4 showed increase in percentage organic matter when compared to P1 and P2.

Total Hydrocarbon content has higher values in soils contaminated with diesel oil and spent oil, with values of 47.08 ± 6.71 mg/kg and 56.72 ± 8.29 mg/kg respectively when compared to T2 (29.08 ± 1.84 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 $p < 0.05$ respectively. 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.

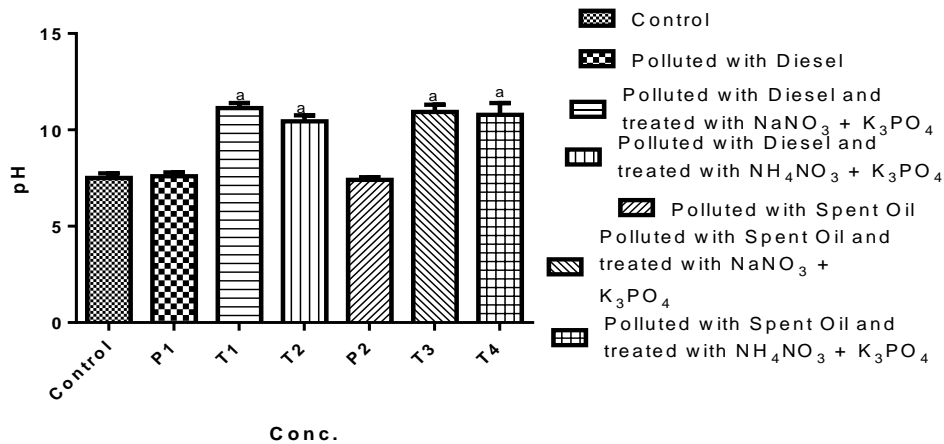


Fig.1: pH of contaminated and treated soils from the study area.

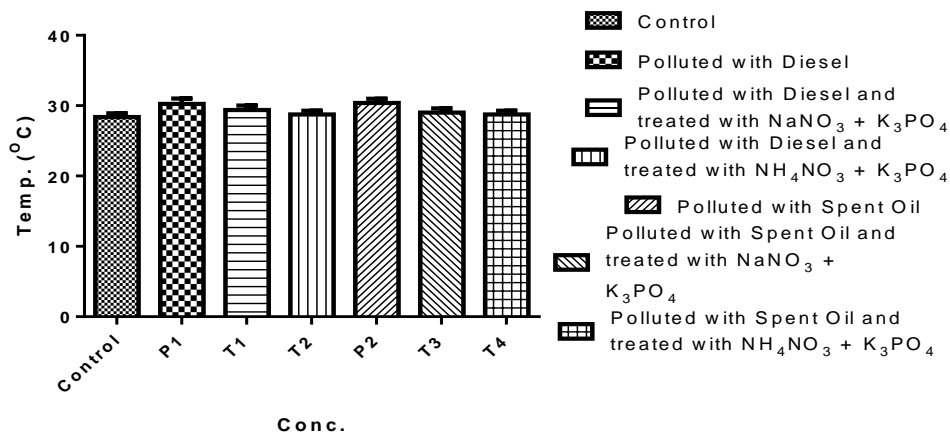


Fig.2: Temp. (°C) of contaminated and treated soils from the study area

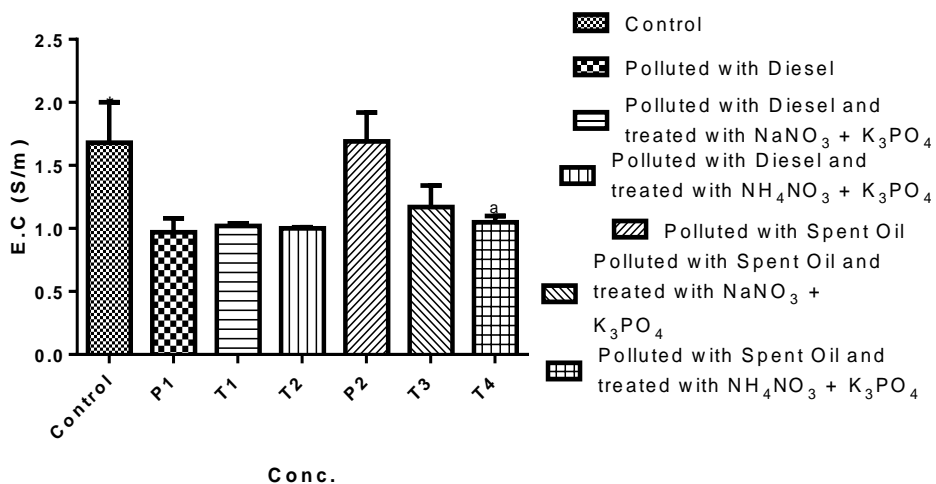


Fig.3: EC (uS/cm) of contaminated and treated soils from the study area.

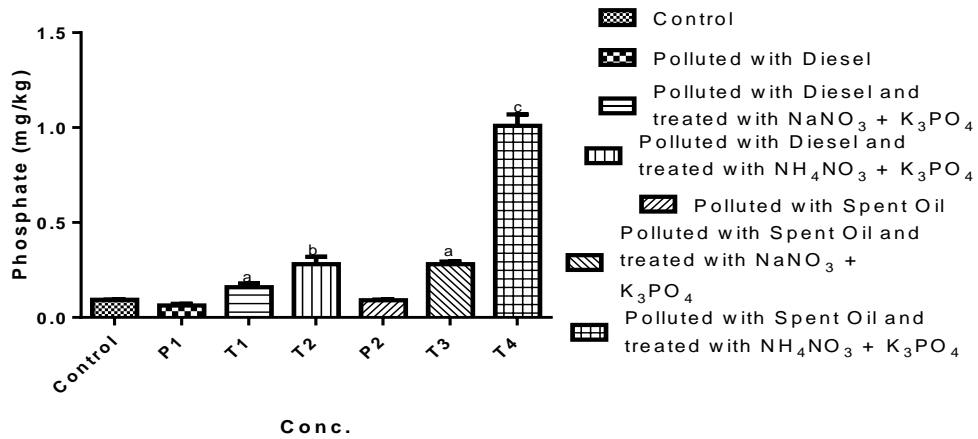


Fig.4: Phosphate (mg/kg) of contaminated and treated soils from the study area

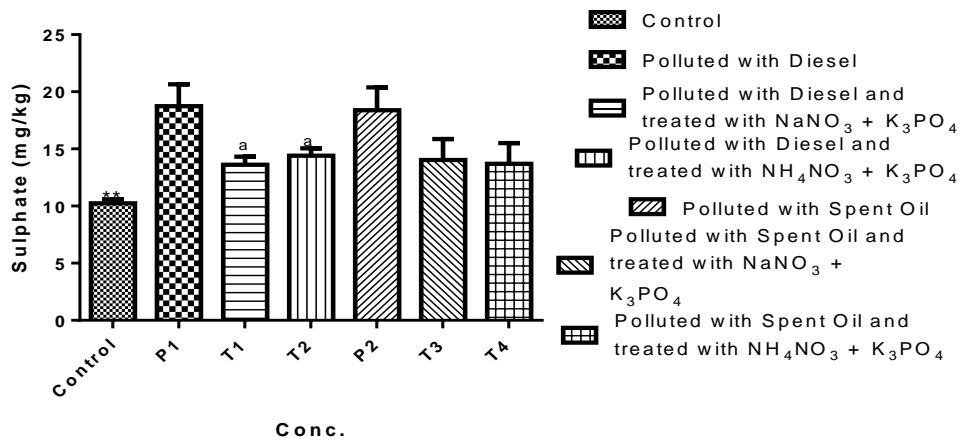


Fig.5: Sulphate (mg/kg) of contaminated and treated soils from the study area

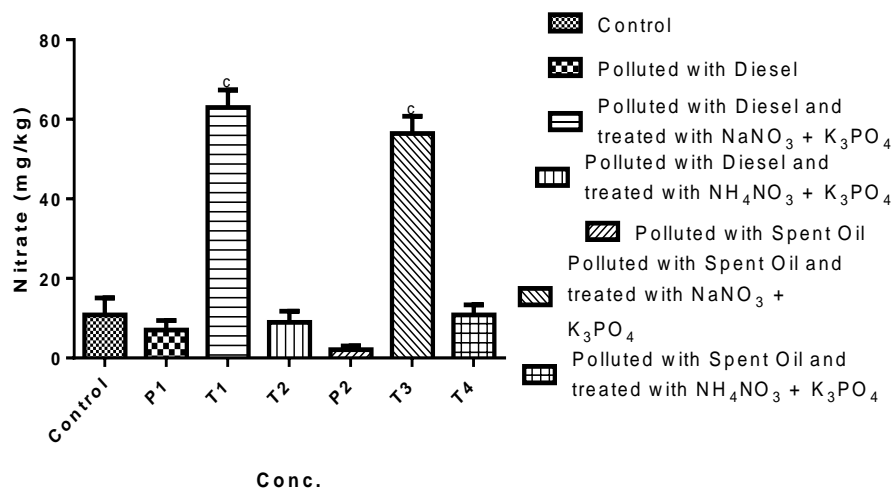


Fig.6: Nitrate (mg/kg) of contaminated and treated soils from the study area

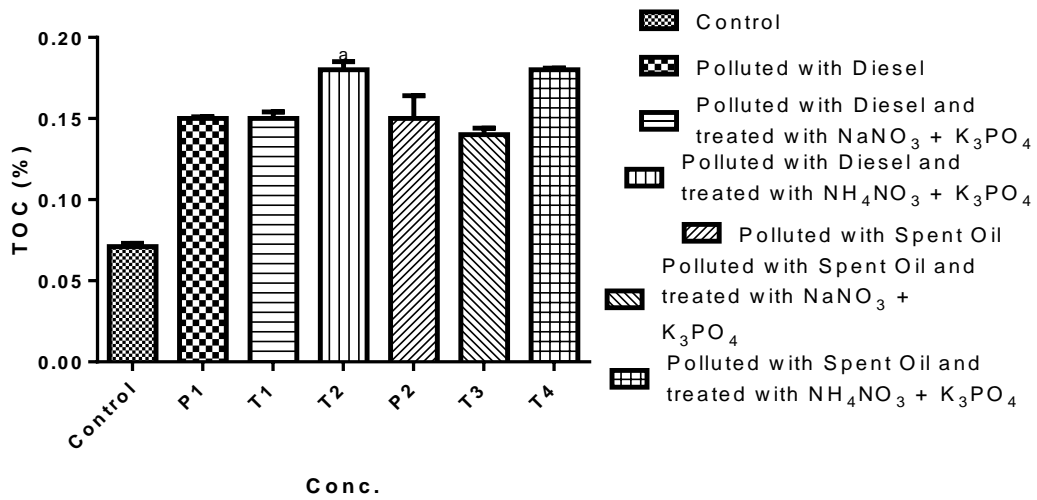


Fig.7: TOC (%) of contaminated and treated soils from the study area

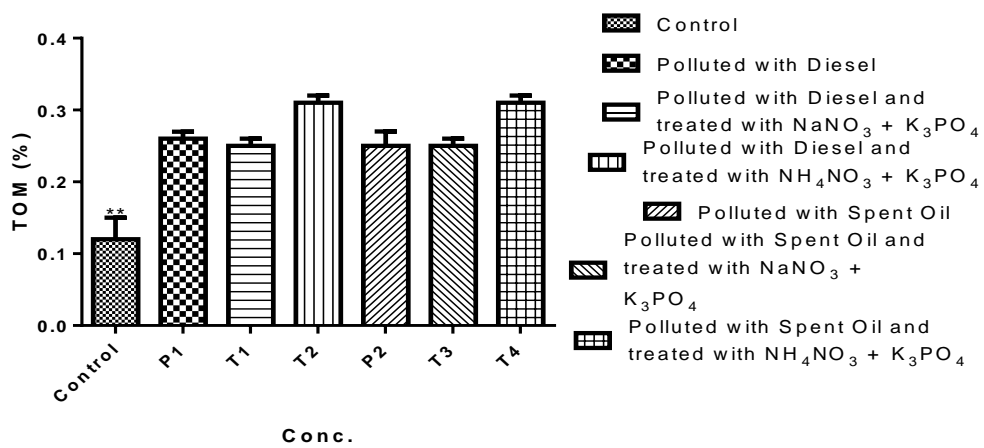


Fig.8: TOM (%) of contaminated and treated soils from the study area.

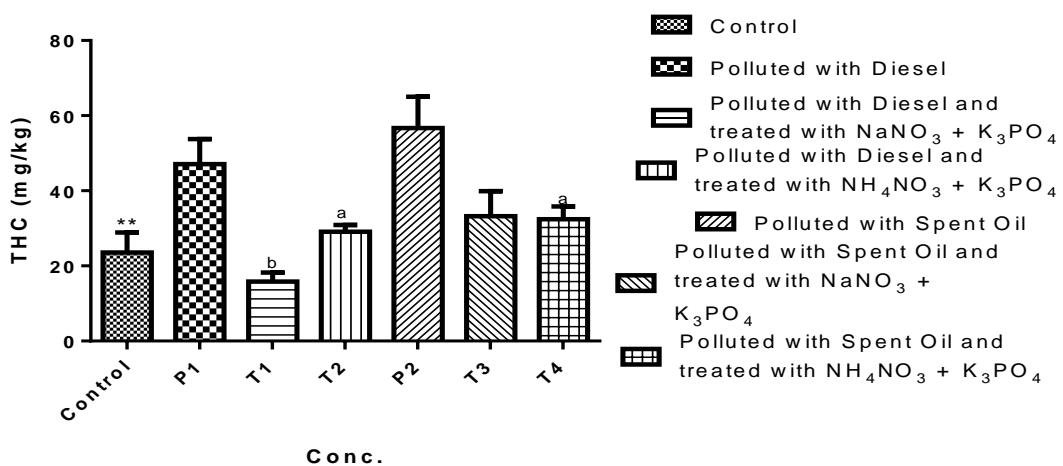


Fig.9: THC (mg/kg) of contaminated and treated soils from the study area

4. CONCLUSION

The best approach towards remediation of soil contaminated with crude oil fractions 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 fractions. This study sought to validate the remediation of Physicochemical Properties of Soils affected by Fuel Spills in Port Harcourt Environment. Careful observations and analysis of contaminated and uncontaminated soils provided insight on the concentration of physicochemical properties of soils. Positive remediation was observed in soils with elevated physicochemical parameters when treated with the ratio of Sodium Nitrate: Potassium phosphate and Ammonium nitrate: Potassium phosphate mixtures, respectively. The study therefore concluded that impact of physicochemical properties on soils aggravated by oil spills were remediated by the application of Sodium nitrate/Potassium phosphate and Ammonium nitrate/Potassium phosphate mixtures, respectively. Thus, establishing the fact that these chemicals can serve as a good option in any remediation process of the soil. However, a mixture of 10% Sodium nitrate to 1% Potassium phosphate remediated better than 10% Ammonium nitrate to 1% Potassium phosphate and it is more economical for remediation of physicochemical properties.

REFERENCES

- [1] American Society for Testing Materials (1999). *Annual Book of ASTM Standards*. 6.
- [2] APHA (1998). *Standard Methods for the Examination of Water and Wastewater*. 20th Edition, American Public Health Association, American Water Works Association and Water Environmental Federation, Washington DC.
- [3] Imasuen, O.I & Omorogieva, O.M. (2013). Sources and Environmental Implication of Heavy Metal Pollution in Plants Grown Around Contaminated Site in Edo State, Nigeria. *Resource Journal in Engineering and Applied Sciences*. USA, 2(5):385-391. www.emergingresources.org
- [4] Okereke, J. N., Obiekezie, S. O. & Obasi, K. O. (2007). Microbial Flora of Oil Spilled Sites. *African Journal of Biotechnology*, 6(8):991-993.
- [5] Onuh, M.O; Madukwe, D.K.; & Ohia, G.U. (2008). Effects of poultry manure and cow dung on the physical and chemical properties of crude oil polluted soil. *Sci. World J.* 3(2): 45 – 50.
- [6] Osuji, L. & Nwoye, I. (2007). Appraisal of the impact of petroleum hydrocarbons on soil fertility: the Owaza experience. *African Journal of Agricultural Research*. 2: 318-324.
- [7] Walkley, A. & Black, I. A. (1934). An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Science* 37:29–38.
- [8] Wang X Y, Feng J, & Zhao J M, (2010). Effects of crude oil residuals on soil chemical properties in oil sites, Momoge Wetland, China. *Environmental Monitoring and Assessment*, 161(1): 271–280.
- [9] Wyszowski, M., Wyszowska, J., Borowik, A. *et al* (2004). Contamination of Soil with Diesel Oil, Application of Sewage Sludge and Content of Macro-elements in Oats. *Water Air Soil Pollution*. 231(546).