

Enhanced Remediation of a Hydrocarbon Polluted Soil

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Abstract: The aim of this study was to use NPKs, saw dust and poultry manure as enhanced remediation techniques of a crude oil polluted soil, using a 42-day study period, time length. Polluted soil samples were collected at 0-10 cm depth from different polluted sites of the same area. Physicochemical parameters such as potassium concentration and total hydrocarbon recorded a decrease at the 6th week, after application and lab testing. Total organic carbon recorded an increase on the 6th week, for treatments containing; PS+SD, PS+NPK and PS+PM. pH ranged between 5.21-10.1. The results suggest that a combination of amendments in the right proportion would be effective in the remediation of crude oil polluted soil.

Key words: Amendments, hydrocarbons, remediation

INTRODUCTION

The public has now come to realise that exploration and exploitation activities in the oil business, generates not only financial benefits but also pollution problems, despite the claims of efficiency and proper control by the oil companies. With an increased demand for petroleum products, which has led to a consequent increase in oil industry activities, the significance and probability of major oil spillage which endangers aquatic and terrestrial environment becomes very high. According to Amakiri and Onofegbara (1983) pollution of any level has a deleterious effect upon the entire ecosystem. Crude oil pollution tends to change the physical and chemical properties of soil, thus indirectly affecting the growth and development of plants, Frankenberger and Johanson (1982). Baker (1970) also concluded that crude oil pollution becomes continuously injurious and adversely affects soil conditions and crop growth. Plice (1948) and Rowell (1977) concurred that oil spillage often result to the destruction of soil properties, microorganisms as well as plant communities. Black (1957) reported the inhibition of root growth due to acidity, which was caused by crude oil contamination. He also demonstrated that growth and development of plants are adversely affected by crude oil pollution, ranging from wilting, chlorosis, tissue and cell maceration, blotching and the collapse of marginal necrotic spots, which have eventually resulted in the death of plants. This study will report the effect of soil amendments, NPK, poultry manure and saw dust on crude oil polluted soils and its characteristics.

MATERIALS AND METHODS

This study was conducted in an oil spill site/farm at IBAA village in Emuoha Local Government Area of Rivers State Nigeria in July 2006.

Area description: The study was conducted in an oil spill site/farmland located at Ibaa village in Emohua LGA of Rivers state, Nigeria. The oil spill was reported to have occurred in June 200, samples were collected at the site in August 2008 when clean up exercise had not commenced.

Materials studied: Materials studied included soil samples from both polluted and unpolluted soils, which were randomly collected with a Dutch auger and trowel at a depth of 0-15 cm from the project site and stored in perforated polythene bags.

Soil amendments: NPK fertilizer was obtained from Agricultural Development Programme, Rivers state, Obia-Akpor LGA. Saw dust was obtained from a milling factory at Elioizu in Obia-Akpor LGA, while poultry manure was collected at a poultry farm in Ghanama, University of Port Harcourt.

Techniques: Soil samples were collected randomly. They were weighed and distributed into perforated bags and allowed for one week before application of amendments. During this period, the collected samples were watered at intervals of 2 days (early mornings and late evenings). After one week, each amendment was carefully weighed and applied to labelled bags, with exception of the control bags. The amendments were homogeneously mixed with the soils in each bag and allowed for one week. No amendment was applied to the control bag.

Methods: Determination of soil physicochemical parameters:

Soil pH: pH of soil samples collected from each bag was determined. Two grams (2 g) of phosphate powdered buffer was dissolved in 200 mL of sterile distilled water, and used to standardise a pH meter at pH 7.0. The reference electrode was aseptically dipped into 50 mL

aliquots containing 1g of each sample. The pH meter was read off and the reference electrode subsequently washed with distilled water.

Determination of total organic carbon: The soil samples (0.05 g), were weighed into digestive flask. Chronic acid mixture, (25 ml), was added to soil samples in the flasks. The flask was heated on a digestion rack for appropriately 30 min. The mixture was then allowed to cool, until just warm and diluted to 100 mL with distilled water. Five milliliters of indicator solution was added and a thick bluish colour developed. This was then titrated with 0.4 m Ferrous Ammonium Sulphate solution, until a greenish colour developed. The volume of 0.4 m, Ferrous Ammonium Sulphate solution gave the titre value. Total organic carbon was determined by;

$$\% \text{ C (ppm)} = \frac{27.5 \cdot \text{titre value} \cdot 0.12}{\text{Weight of sample digested}}$$

Nitrate: Here the Brucine method was used. Calometric procedures were applied to measure the yellow nitro derivatives formed between the reactions of nitrate ions with brucine in the presence of a strong acid solution such as H_2SO_4 . The color that developed was measured as 470 nm wave length and the nitrate concentration extrapolated from a standard nitrate curve. One gram of soil sample was weighed; 10 mL of water was added to it. One milliliter of the sample was pipetted into a clean test tube and then 0.5 mL of 2.5% brucine solution in acetic acid was added to the tube. After this, 2 mL of concentrated H_2SO_4 was added and thoroughly mixed. The tube was then allowed to stand for about 15-30 min. The color that was developed was measured at 470 nm using distilled water as a blank. The nitrate concentration in the sample was extrapolated from standard nitrate graph, prepared from, nitrate stock solution of 0.1 mg/mL. Concentration nitrate was determined using the formula:

$$\text{NO}_3 = \text{Nmg/L} = \frac{\text{C (mg)} \cdot 100}{\text{Aliquot.vol. (mL)}}$$

Potassium: Samples were measured at 760 nm wavelength. A calibration curve was prepared from the standard range by setting the top standard to a suitable scale deflection and the ppm standard to zero. The sample solution was aspirated into the flame under the same condition as the standards. The top zero and intermediate standards were checked frequently as recommended by the instrument employed. The burner and atomizer were flushed frequently with water, particularly at the end of each run. The calibration curve was used to determine ppmK, in the sample solution. Blank determination using distilled water, was carried out in the same way and subtracted were necessary:

$$\text{K(mg/L)} = \frac{\text{C(ppm)} \cdot \text{Solution Volume (mL)}}{10^4 \cdot \text{Sample Weight (g)}}$$

Phosphate: One gram of soil sample each was made up to 50 mL with distilled water. The solution was pipetted into clean dry test tube. Phenolphthalein indicator solution, (0.05 ml), was added, drop wise to give a bluish color. Eight milliliters of combined reagent was added and thoroughly mixed. The mixture was allowed to stand for at least 10 min. The absorbances of the samples were taken thereafter at 700 nm using reagent blank as the reference solution. Phosphorous concentration in the soil samples was extrapolated from standard curve and calculated using the relationship:

$$\text{mg P/1000 g of sample} = \frac{200 \cdot 100 \cdot \text{Conc.from graph}}{1000}$$

Total hydrocarbon content: The method employed was the photometric method adopted from Shell Manual of the American Petroleum Institute (1980). Soil samples, (0.1 g), was mixed with 10 mL of carbon tetrachloride solution. This mixture was stirred and decanted using a separate funnel into a glass capped container. Clean tap water was added and shaken vigorously until all silt materials in the sample were displaced. The mixture was allowed to stand out and the carbon tetrachloride phase decanted into a clean conical flask. Enough Na_2SO_4 , (anhydrous), was added and shaken vigorously to remove all traces of water that may still have been present in the mixture. The resultant clear solution was analysed spectrophotometrically at 420 nm using Carbon Tetrachloride Solution as a blank. Hydrocarbon (oil and grease), concentration in the samples were extrapolated from a standard curve and calculated using the relationship:

$$\% \text{ Crude oil (ppm)} = \frac{\text{Conc.from graph} \cdot \text{T.V.S.E}}{\text{Weight of sample (mg)}}$$

where, T.V.S.E. is total volume of solvent extract (10 mL).

RESULTS AND DISCUSSION

The concentration of potassium ion in the soil samples is shown in Fig. 1. There was a general trend of an increase on the 3rd week and a decline on the 6th week, irrespective of the treatment combination. But the concentration was higher in polluted soil + saw dust, polluted soil + poultry manure and polluted soil + saw dust + poultry manure + NPK.

Figure 2 shows the total organic carbon in the soil samples after amendment. The total organic carbon was higher after 3 weeks then declined for the treatments: PS+NPK, PS+NPK+SD and PS+SD. On the contrary, it

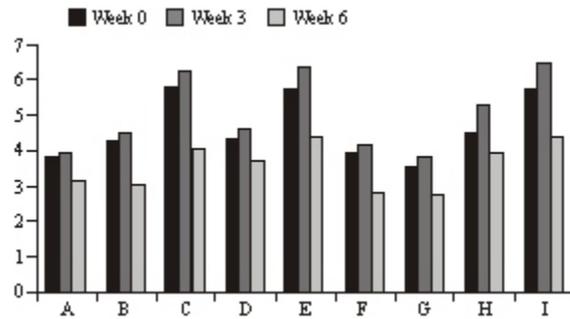


Fig. 1: Effect of amendments on potassium concentration (mg/kg)
 A: Unpolluted soil (control 1); B: Polluted soil (control 2); C: PS+SD; D: PS+NPK; E: PS+PM; F: PS+NPK+PM; G: PS+NPK+SD; H: PS+SD+PM; I: PS+SD+PM+NPK

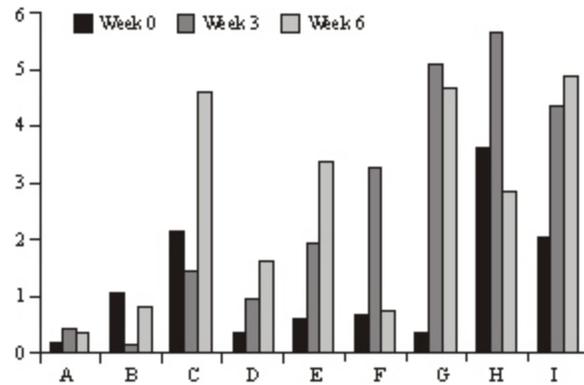


Fig. 2: Effect of amendments on total organic carbon (%)
 A: Unpolluted soil (control 1); B: Polluted soil (control 2); C: PS + SD; D: PS + NPK; E: PS + PM; F: PS + NPK + PM; G: PS + NPK + SD; H: PS + SD + PM; I: PS + SD + PM + NPK

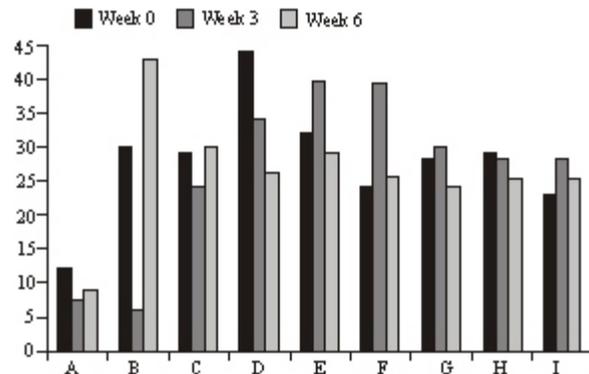


Fig. 3: Effect of amendments on total hydrocarbon
 A: Unpolluted soil (control 1); B: Polluted soil (control 2); C: PS + SD; D: PS + NPK; E: PS + PM; F: PS + NPK + PM; G: PS + NPK + SD; H: PS + SD + PM; I: PS + SD + PM

increased on the 6th week for the following treatments: PS+SD, PS+NPK and PS+PM.

The total hydrocarbon (Fig. 3) in the soil sample containing polluted soil + NPK was considerably high at week 0. However there was an accompanying decrease

with time. In samples containing polluted soil + poultry manure, polluted soil + NPK + Poultry manure, polluted soil + NPK + saw dust and polluted soil + saw dust + poultry manure + NPK there was a slight increase in week 3 and then a decrease in week 6 indicating that there

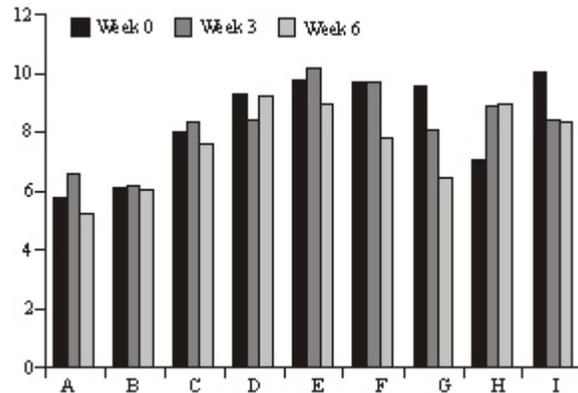


Fig. 4: Effect of amendments on pH of polluted soil
 A: Unpolluted soil (control 1); B: Polluted soil (control 2); C: PS + SD; D: PS + NPK; E: PS + PM; F: PS + NPK + PM; G: PS + NPK + SD; H: PS + SD + PM; I: PS + SD + PM + NPK

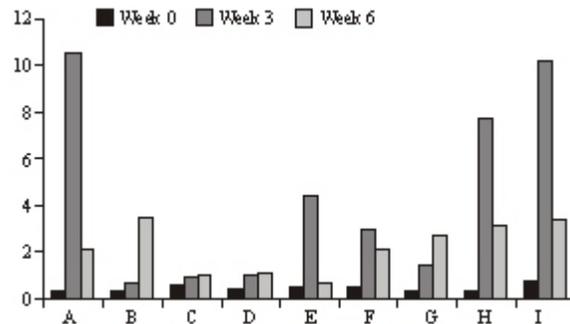


Fig. 5: Effect of amendments on soil nitrogen
 A: Unpolluted soil (control 1); B: Polluted soil (control 2); C: PS + SD; D: PS + NPK; E: PS + PM; F: PS + NPK + PM; G: PS + NPK + SD; H: PS + SD + PM; I: PS + SD + PM + NPK

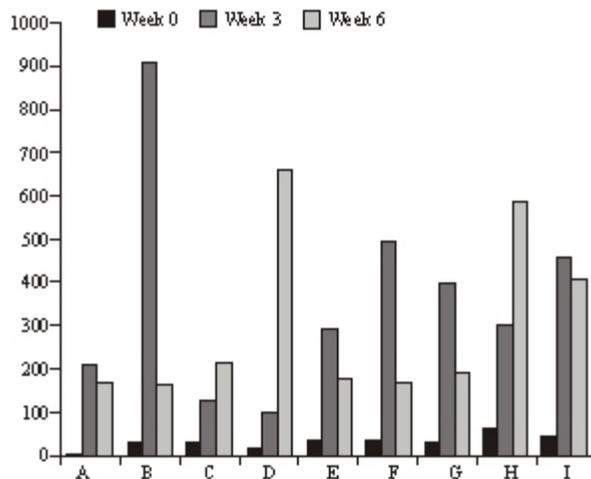


Fig. 6: Effects of amendments on phosphate (mg/kg)
 A: Unpolluted soil (control 1); B: Polluted soil (control 2); C: PS + SD; D: PS + NPK; E: PS + PM; F: PS + NPK + PM; G: PS + NPK + SD; H: PS + SD + PM; I: PS + SD + PM + NPK

would still have been a minimal level of microbial activity.

The results of soil pH during the period of sampling are presented. The pH was acidic between 5.5 and 6.5 for

unpolluted and polluted soil. Addition of amendments made the soil slightly alkaline (Fig. 4).

This shows the concentration of nitrogen in the soil samples. There was no significant increase in week 0. Higher concentration was observed mostly after 3 weeks (Fig. 5).

There was little or no phosphate at the beginning of the study but after 3 weeks, it increased (Fig. 6).

The use of amendments in bioremediation as effective and economic tools of post oil spill clean up, is yet to be fully exploited in Nigeria. Even when the soil is not polluted, there still lingers the limitation problem in ecosystems of nitrogen and phosphorous. This study lasted for 6 weeks. The pH value for polluted and unpolluted soil samples generally were within the acidic range, (5.5-6.5). On application of amendments, a slight shift towards alkalinity was observed. This trend has been reported by Bartha and Bossert (1984). Alkalization by these amendments was observed mostly at week 0 and week 3. Dibble and Bartha (1979) reported a pH range of 6.5-8.0, for optimum mineralization of hydrocarbons. The pH values thus recorded during this study are suitable for bioremediation. The total organic carbon content of the soil was significantly low at week 0, indicating that biodegradation actually took place. There was a reduction in phosphate level in the soil at week 0. The polluted soil sample had the highest phosphate concentration at week 3. Kinako (1981), also reported that adjustment of C:N:P ratio in an oil contaminated soil was highly beneficial to soil biodegradation, but only after the inherently low pH of the soil was adjusted upward. The application of amendments therefore must be responsible for the subsequent increase in week 3 and week 6 in phosphate content of the soil. A similar trend was observed for nitrogen.

CONCLUSION

Generally the total hydrocarbon content increased in soil samples containing various amendments when compared to the unpolluted soil control. This can be assumed to be as a result of microbial activity in the soil.

Although factors such as runoff, flood and leaching, evaporation and photo-oxidation can also effect hydrocarbon removal, Atlas and Bartha (1992). Therefore, the increase or decrease in total hydrocarbon content is dependent on the type of amendment.

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