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# Bioamendment of petroleum contaminated ultisol: effect on oil content, heavy metals and pH of tropical soil

E. D. Udosen[1], J. P. Essien[2], R. M. Ubom[2]

(1. Department of Chemistry and Biochemistry, University of Uyo, Nigeria; 2. Department of Botany and Microbiology, University of Uyo, Nigeria)

**Abstract**: The effect of organic amendments on the oil content, heavy metals concentration and pH of petroleum contaminated sandy loam ultisol obtained from Rumuekpe oil field in Emohua Local Government Area of Rivers State, Nigeria was determined. Petroleum contaminated soils were treated with wood ash, compost and sawdust. The addition of organic amendments resulted in a significant (at 95% probability level) decrease in oil content by 92% for composting, 81% for soil treated with sawdust and 58% for soil with ash supplementation, over 6 months. The effect of treatments on the iron (Fe), copper (Cu) and lead (Pb) concentration was significant at $P<0.001$. The remediation also affected the pH of soil. This initial pH of 5.6 was depressed by the application of compost and sawdust supplements respectively to a final pH of 5.2 and 5.3. On the other hand, amending the soil with wood ash raised the pH from 5.6 to 6.2. Increased acidity caused a decrease in the heavy metals concentration in the contaminated soil. Soil treatment with compost generally gave the best remediation results, followed by sawdust and then ash. Adjusting the pH of oil contaminated soil to high acidic levels may promote the availability and migration of heavy metals in remediated soils and not necessarily the rate of oil mineralization.

**Key words**: bioamendament; tropical soil; Nigeria

## Introduction

Most soil pollution situations involve several pollutants acting simultaneously. The practical assessment of the overall toxicity has therefore remained a major problem. Among the negative effects of exploration and production activities in oil producing communities in Nigeria that are evident over the years are contamination of soil and ground water by hydrocarbons (Odu, 1981; Ewa-Oboho, 1994). Other pollutants such as heavy metals are also commonly associated with petroleum industry (Ijah, 1992).

Metals found in exploitation and production wastes include Cr, Cd, Pb, Cu, Zn and Ba (EPA, 1987; Ijah, 1993). The availability of these metals and their potential to migrate have been reported to depend on pH, redox potential and metals concentration (Holliday, 1994). In an earlier investigation, Freeman and Deuel (Freeman, 1984) revealed that the availability of metals in petroleum contaminated soils is inversely related to pH except Ba, which solubility is directly related to pH. The same authors also reported that controlling pH, incorporation of drilling clays in soil and improving soil structure by organic amendment provided aviable method of remediating soils contaminated by hydrocarbons and associated metals. Miller and Honarvar (Miller, 1975) demonstrated that soils having high organic matter content and moderate concentration of clay appear to be less sensitive to high sodium and soluble salt concentration than the coarser and textured soils.

Heavy metals are known to exert adverse effect on biological processes in general (Wilber, 1971; Esenowo, 1995; Udosen, 1998). Dibble and Bartha (Dibble, 1979), Odu (Odu, 1981), Ijah and Okang (Ijah, 1993) have reported the effect of metals on the degradability of bacteria in soil. Their findings suggest that the metals from in soluble complexes in acidic soil and this may increase their potential of interfering with metabolism (Murphey, 1984; Moseley, 1984). However, little or no attention has been given to the effect of organic amendments on the oil content and heavy metal concentration in petrolum contaminated soils, nor has the effect of soil pH fluctuations on the level of metals in oil polluted soils been evaluated. The knowledge of these are of outmost importance to select optimum remediation strategies.

# 1 Materials and method

Oil-spilled soil samples from Rumuekpe oil spilled site in Emohua local government area of Rivers State, Nigeria were used for this study. Emohua Local Government is located within the rainforest zone of Nigeria.

## 1.1 Physicochemical analysis of soil

The soil properties were determined using standard procedures(Allison, 1965; AOAC, 1984; Udo, 1986). Soil extracts were prepared by rotating upside down 100g of the oil contaminated soil in 200 ml of deionized water for 30 minutes. The pH of the soil was measured by Beckman's glass electrode. From the soil extract, total nitrogen was determined by Microkjeldahl method and organic carbon by Walkley-Black method(Udo, 1986). Available phosphorus in soil sample was determined after extraction with 0.5 mol/L $NaHCO_3$ solution while exchangeable cations were determined after extraction with 1 mol/L ammonium acetate solution(AOAC, 1984; Udo, 1986). Soil particle size distribution was determined by the hydrometer method (Udo, 1986).

## 1.2 Chemical analysis of organic amendments

The organic amendments used were five months old compost mainly from plants of the family Asteraceae in addition to wood ash and sawdust collected within the locality of study. Fresh weight of each amendment was recorded before drying to constant weight in a Gallenkamp oven at 60℃ for three days and dry weight recorded. The difference between fresh and dry weight of each amendment gave the amount of moisture content from which the percentage moisture of each amendment was calculated.

Sample of each amendment(10g) was used for total nitrogen determination by micro-kjeldahl method(Udo, 1986). This was multiplied by 6.25 to obtain the crude protein content. Crude lipid was determined from 5g of each amendment adopting the vanadomolybdate method (AOAC, 1984). The water-soluble phosphate was determined calorimetrically by the molybdenum blue method (Jokobsen, 1982; Udo, 1986). Lignocellulose content of the amendments was measured by Soxhlet's technique (Garg, 1985) while the proportion of the readily soluble components (alcohol soluble sugars) was determined by Benedict's quantitative analysis after extraction with aqueous methanol(Rajhan, 1986). Total organic carbon was determine by Walkley-Black method and mineral matter by dry ashing in a muffle furnace using 10g of each amendment(Udo, 1986). The pH of each amendment was measured in 1:1 water: amendment ratio using Beckman's electrode.

The total number of aerobic bacteria in the organic amendments was enumerated by the viable plate count method. Serial dilutions ranging from $10^{-1}$ to $10^{-10}$ of the amendments were prepared. Volumes (1 $cm^3$) of each dilution were plated on Bacto plate count agar(oxoid). Triplicates of each dilution ($10^{-1}$ to $10^{-7}$) were prepared and incubated at 28℃ for 36 hours before enumeration.

## 1.3 Soils amendment

The oil polluted soils were put into rectangular plastic pots with surface area of 60 cm × 35 cm and a depth of 40 cm. The organic amendments were incorporated into the test soil by base application in 3:2 soil-amendment mixture. The rectangular pots had holes in their bottom and were placed in saucers and watered semi automatically with deionized water from below. Excess water was collected from a pipe stubs at the sides of the saucers.

The soil treatments were carried out during the rainy season between May and October 1995. The amended soil was allowed to age for two months(May to June), before incubation for a period of 4 months, giving a total remediation period of 6 months.

## 1.4 Determination of oil content of test soil

Oil content was determined by Soxhlet extraction(McGill, 1977). The soil after extraction was dried and the oil content calculated as a percent of the dry soil weight. Prior to extraction, all samples were ground in a warring lender to allow a uniform sub-sample to be removed. The analysis was conducted in duplicates every four weeks within 4 months.

### 1.5 Determination of pH and heavy metals content of test soils

The oil-spilled soil microcosms in wooden boxes were sampled at specific depth of 5 cm, 4 weeks after the organic amendments were added. The soils were air dried and further ground to pass through 1 mm mesh sieve. Soil pH was determined in 1:1 soil-water suspension using a Pye-Unicam model pH meter (AOAC, 1984). The total Cu, Pb and Fe concentrations in the soil samples were extracted and determined by atomic absorption spectrophotometer (Pye Unicam Model SP 192). These analyses were repeatedly carried out after every month during the study period.

### 1.6 influence of pH adjustments on concentration of metals in amended soils

Variation in the pH of oil-spilled soil was created by providing specific pH amendments to soil samples under the different (ash, compost and sawdust) treatments. Adjustments in soil acidity were obtained by spreading the pH amendments on the soil surface and physically mixed by disking (Holliday, 1994). Agricultural limestone ($CaCO_3$) was applied to adjust excess acidity (low pH) and elemental sulphur (S) was used to adjust excess alkalinity (high pH). Analysis for the metal concentration at different pH levels was carried out on monthly basis. This was also conducted on untreated soil contaminated with oil to serve as control.

Analysis of variance (ANOVA) was performed on the mean values of heavy metal concentrations under different treatments using the method described by Sokal and Rohlf (Sokal, 1969).

## 2 Results

**Table 1 Some physicochemical properties of test soil (Ahoada soil, Nigeria)**

| Soil properties | Contents |
|---|---|
| pH | 5.6 |
| Organic carbon, % | 4.74 |
| Total nitrogen, % | 0.07 |
| C/N ratio | 68.1 |
| Avail-P, ppm | 6.07 |
| K, meq/100g | 3.3 |
| Na, meq/100g | 6.8 |
| Mg, meq/100g | 6.8 |
| Ca, meq/100g | 3.9 |
| Sand, % | 83.6 |
| Salt, % | 6.5 |
| Clay, % | 10.6 |

Notes: values are mean of duplicate determinations

The characteristics of the hydrocarbon contaminated soil are given in Table 1. According to Dogue, Hartley and Watson soil classification scheme, the soil is classified as a ferralitic sandy loam ultisol (D'Hoore, 1964). Based on the following characteristics: 83.6% sand, 10.6% clay and 6.5% silt. The organic carbon content was 4.74%, total nitrogen, 0.07%, while the C/N ratio estimated was 68.1. The soil also contained 6.07 ppm of phosphorus. The concentrations of exchangeable bases were 3.3, 6.8 and 3.9 meq/100g for K, Na, Mg and Ca respectively. The soil pH measured in soil-water suspension was 5.6, while the oil content was 17.4%.

The nutrient properties of the organic amendments are presented in Table 2. Of the three amendments, woodash had the highest value of mineral matter, pH, total carbon and C/N ratio. Compost had the highest moisture content, total nitrogen, crude protein and alcohol soluble sugars. Sawdust had the lowest of all properties except lignocellulose. Crude protein, crude lipid, lignocellulose and soluble sugars were not present in woodash component, which also contained the least number of heterotrophic bacteria.

The addition of organic amendment caused a significant (at 95% probability level) reduction in oil content of the petroleum contaminated soil. Four months after organic amendment, amending the soil with compost induced a reduction in soil oil content from 17.4% to 1.34%, representing about 92.2% reduction from the initial oil content of the soil. This varied remarkably from 81.3% and 58.3% reduction in soil oil content caused by the application of sawdust and ash respectively (the figure is omitted).

Table 2 Nutrient properties of the organic amendments

| Properties | Amendments | | |
|---|---|---|---|
| | Woodash | Sawdust | Compost |
| Alcohol soluble sugar, % | – | 3.94 | 15.42 |
| Crude lipid, % | – | 5.46 | 6.04 |
| Crude protein, % | – | 16.47 | 19.21 |
| Lignocellulose, % | – | 78.20 | 56.10 |
| Mineral matter, % | 98.80 | 12.47 | 14.01 |
| Moisture content, % | 1.24 | 49.14 | 64.40 |
| pH | 7.9 | 5.7 | 5.1 |
| P-water soluble, ppm | 8.12 | 8.01 | 6.82 |
| Total organic carbon, % | 82.4 | 20.61 | 44.04 |
| Total nitrogen, % | 0.002 | 2.61 | 3.05 |
| Microbial count, $\times 10^5$ cfu/g | 13 | 28 | 31 |

Notes: value are mean of duplicate determinations

The Fe, Cu and Pb concentrations in the petroleum contaminated soil were slightly affected by the organic amendment. However, the Pb concentrations in soil was seemingly more affected by compost treatment(Fig.1). The effect of the organic amendments on soil pH varied with the type

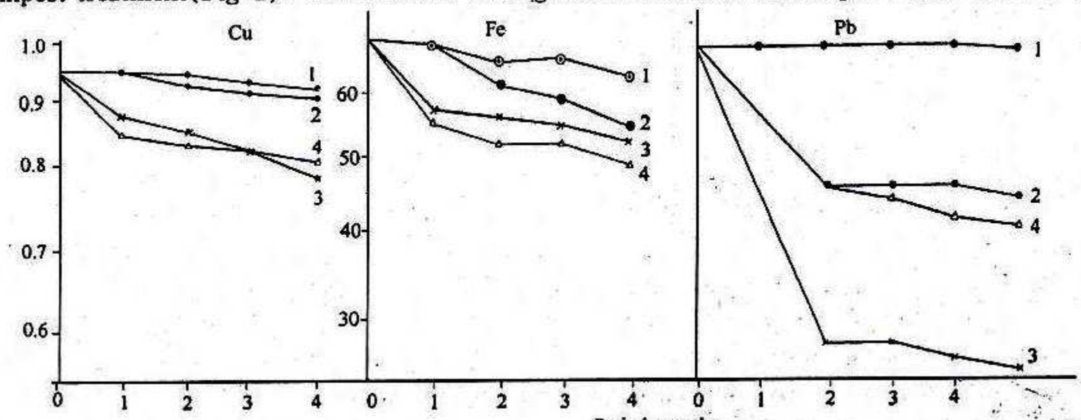


Fig.1 Monthly changes in heavy metals concentration of bioremediated soils
1.control; 2.ash; 3.compost; 4.sawdust

of amendment incorporated into the soil. The acidic level of the soil (pH 5.6) was altered by ash towards alkalinity (pH 6.2) while soils amended with compost and sawdust became more acidic(Fig.2). Mean pH of 5.3 and 5.2 were recorded respectively for sawdust and compost over 4 months of remediation. Adjusting the pH of amended soil also affected the amount of metals in soil. Analysis of variance revealed that both the organic amendment and changes in pH have significant effect on the concentrations of Cu, Fe and Pb in oil polluted soil (Table 3).

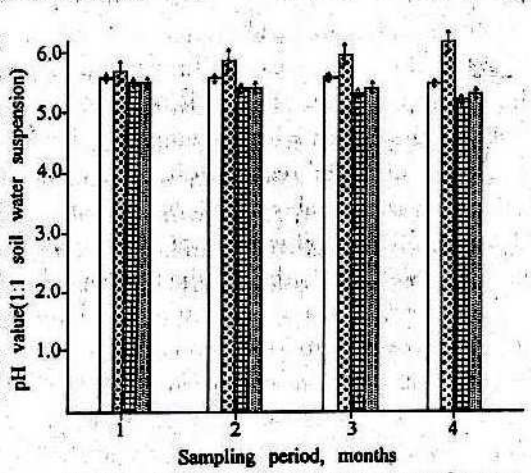


Fig.2 Monthly fluctuations in pH level of remediated soils. The effect of amendments on pH was significant at 95% probability level. Each value is a mean + SEM( ) of 3 replicates

## 3 Discussion

The high level of oil content (17.4%), acidity (pH 5.6), C/N ratio (68.1%) and the relatively low nitrogen and phosphorus levels of the Emohua soil(Table 1) investigated are indications of a tropical soil that is severely contaminated with hydrocarbons. High levels of acidity and carbon concentration are often associated with oil contaminated tropical a soils(Odu, 1981). Similarly Rhykerd *et al*. (Rhykerd, 1995) noted that nitrogen and phosphorus are in relatively short supply in oil contaminated soils, and are needed to complement the carbon supply for development of microbial biomass.

**Table 3 Mean( ± *SE*) concentrations of heavy metals at different pH levels in amended soil**

| Treatment | pH | Heavy metal concentration, ppm | | |
|---|---|---|---|---|
| | | Cu | Fe | Pb |
| Control (Untreated oil) | 5.6 | 0.95±0.02 | 63.24±1.51 | 65.82±0.47 |
| | 4.5 | 0.92±0.01 | 55.11±1.29 | 41.72±0.53 |
| Ash | 5.0 | 0.93±0.00 | 55.66±1.04 | 42.78±0.59 |
| | 5.5 | 0.94±0.01 | 59.00±1.85 | 45.02±0.49 |
| | 6.0 | 0.94±0.00 | 59.52±2.01 | 41.79±3.57 |
| | 4.5 | 0.79±0.02 | 48.25±2.73 | 30.51±0.44 |
| | 5.0 | 0.83±0.01 | 51.86±0.66 | 30.97±0.36 |
| Compost | 5.5 | 0.85±0.02 | 53.29±0.98 | 31.00±0.31 |
| | 6.0 | 0.85±0.01 | 52.55±0.50 | 31.96±0.85 |
| | 4.5 | 0.88±0.01 | 50.93±1.80 | 39.44±0.52 |
| | 5.0 | 0.90±0.01 | 53.39±1.81 | 42.18±1.65 |
| Sawdust | 5.5 | 0.92±0.01 | 53.99±1.47 | 45.21±1.87 |
| | 6.0 | 0.92±0.00 | 54.10±1.42 | 46.66±1.69 |
| Significance | | ** | ** | ** |

Note: ** significant at $P<0.001$

The objective of applying organic amendments to hydrocarbon contaminated soils is to protect the soil structure and provide utilizeable nutrients to the indigenous micro-organisms including complex hydrocarbon degraders. The reduction of oil in amended soils might be due to the supply of nutrients which were otherwise limiting. Atlas and Bartha(Atlas, 1973) and Nyborg and McGill (Nyborg, 1975) observed that the application of nutrients particularly nitrogen and phosphorous would accelerate the decomposition of crude oil in soil. Atlas (Atlas, 1995) reported that the growth and proliferation of indigenous microbial population in hydrocarbon contaminated soil are usually enhanced by the presence of nitrogen and phosphorus. These elements are relatively in short supply in oil polluted soils.

The concentrations of nitrogen and phosphorus are remarkably high in compost(Table 2). The simulating effects of these elements on micro-organisms including the oil degraders in soils is probably the reason why amending the soil with compost gave the highest level of oil mineralization in treated soil. The reduction in oil content of soil treated with compost was more drastic and the result showed that about 92% of oil weight had been removed after incubation for 6 months. About 81% and 58% of oil were respectively removed from soils treated with sawdust and ash, while the untreated soil still harbored about 91% oil by weight (representing only 9% reduction of oil) for the same period of remediation. The slight reduction in oil content of the untreated soil(control) may be attributed to loss of volatile fraction of oil and intrinsic biodegradation. The results are in line with observations of Jobson *et al*.(Jobson, 1974) and Fyock *et al*. (Fyock, 1991). Fyock *et al*. recorded great success with compost treatment of oil contaminated soil in Windrow. A reduction in oil content, from 10% to 0.6% was obtained in slightly more than 30 days. Under compost treatment all the soluble nitrogen compounds and the proteins were decomposed. Typically half the nitrogen is usually transformed to ammonia and lost by volatilization. The remaining nitrogen is often used by the microbes to build up microbial proteins, commonly called biomass (Jakobsen, 1995).

Amending the oil contaminated soil with organic nutrient supplements had little effect on the concentrations of Fe, Cu and Pb in soil (Fig. 1). The concentrations of Fe and Cu were reduced slowly and not below 40% over 6 months of remediation with both sawdust and woodash, except in the composed soil. On the other hand, compostation recorded a much more remarkable effect on Pb concentration reducing it to about 15% over a period of 6 months. The results of this study is in agreement with observations of Holliday and Deuel (Holliday, 1994). Holliday and Deuel (Holliday, 1994) attributed such reduction in amount of metals to increase in soil acidity or reduction in redox potential of soil. It has also been reported that nutrient rich bacterial growth substrate can complex heavy metals and remove them from solutions, thus reducing the appearance concentration of the metals in the substrate(Murphy, 1984; Duxbury, 1986).

Variation in the pH of the amended soil was not unexpected and could be ascribed to differences in pH status of the organic amendments(Table 1). The increase in acidity of soils under compostation and sawdust treatment could be attributed directly to the decomposition of the organic compounds by micro-organisms. The organic acids that might have evolved from the degradation process would depress pH from the original levels(Nyborg, 1975) while the high mineral matter of wood ash may have contributed to the decrease in the acidity of soils treated with ash. Ashing raised the pH of the soil from 5.6 to 6.2. Statistical analysis (ANOVA) have shown that changes in pH of soil amended with organic nutrient supplements affected the concentration of heavy metals significantly(Table 3). The reduction in metal concentration increases with increase in soil acidity. The effect was quite remarkable in soil under compostation. The pH of the soil affects microbial activity, availability of nutrients, immobilization of metals, rates of abiotic transformation of organic waste constituents and soil structure (Pope, 1993). A pH range of 6.8 is considered optimum for bioremediation in most cases. Most metals tend to be less mobile in high pH soils. They form insoluble complexes in such soils and the potential of heavy metals to migrate in soil has been reported to be primarily controlled by pH (EPA, 1987; Holiday, 1994).

The degree of oil decomposition was lower in soil treated with ash mainly due to lack of nutrients and low microbial population (Table 2). The shift of pH towards alkalinity might also have affected the rate of heavy metal migration in soil amended with ash. On the other hand, the high acidity of soil amended with compost and sawdust would reduce the amount of metals but the rate of hydrocarbon degradation might not increase despite their microbial quality microbial(Table 2).

It is of great value to the problem of oil contaminated environment to use organic amendment for protection of soil structure and for supply of microorganisms including the hydrocarbon-degraders to soil. In order to achieve result, it is important to know the chemical process that occur during oil decomposition as well as the physical and chemical quality of the amendment. Compostation of petroleum contaminated soils with plant material promotes not only the microbial population of soil but also creates an acidic condition that would enhance the migration of metals and or formation of insoluble complexes that may not hamper biological activities in hydrocarbon contaminated soils. However, the usefulness of extra amendments would depend on the character of each individual spill sites.

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