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EVALUATION OF POULTRY MANURE-BIOCHAR ADDITION TO STIMULATE OIL DEGRADATION IN SOIL

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Abstract
In this study, remediation of heavy metals; arsenic, cadmium, chromium, copper and lead, and petroleum hydrocarbons in co-contaminated soil using in situ application of admixtures of poultry manure and termite mound soil was examined. The contaminated soil with total heavy metals content, M_{Tot} 110.69±3.08 mg.kg^{-1} (As 8.00±0.36 mg.kg^{-1}; Cd 10.83±0.33 mg.kg^{-1}; Cr 20.90±0.56 mg.kg^{-1}; Cu 43.43±0.99 mg.kg^{-1} and Pb 25.45± ±0.85 mg.kg^{-1}) and total petroleum hydrocarbons content 208.30±0.62 mg.kg^{-1} was treated with admixtures of poultry manure and termite mound soil of various compositions (0 – 100 wt% poultry manure) and durations (30 – 120 days) of amendment application. Reductions in the levels of total-extractable and bioavailable metal fractions and in residual total petroleum hydrocarbons, plant (maize) uptake and transferability of heavy metals and changes in soil enzyme activities were used as indicators of remediation end-point. It was found that in comparison with unamended soil, marked reductions (in the range 64 -89%) were associated with poultry manure/termite mound soil application to the contaminated soil. The reduction in bioavailable metal fraction following amendment application was reflected in corresponding reduced plant uptake, 18-fold by maize roots and 25-fold in transferability to maize shoots as a result of the application of poultry manure/termite mound soil to the contaminated soil. Degradation of petroleum hydrocarbons varied in apparent dependence on the poultry manure content of the amendment and was almost quantitative (95%) with application of amendment (100 wt% poultry manure) and duration of 120 days. Increased levels of soil enzyme activities of several order of magnitude (67 – 500%) in comparison with unamended soil accompanied application of poultry manure/termite mound soil amendment to the contaminated soil. Restoration of soil quality (measured in terms of enzyme activities) depended on the level of poultry manure component of the amendment material.

Keywords: contaminated soil, remediation, amendment application, metals, petroleum hydrocarbons

Introduction
The use of stabilizing materials for remediation of inorganic (mainly metals and metalloids) and organic contaminants in soils has gained broad acceptance as remediation technology [1]. The overall objective of amendment technologies is to sequester and stabilize contaminants in soils and sediments in order to reduce their ability to partition to water or biota and thus their potential for transport and toxicity. Numerous materials, including silicate, clay materials, forms of phosphate, carbonate, sulphate, oxide or hydroxide, organic residues (biosolids such as manure or

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sewage sludge) [2] have been investigated for application to surface soils and surface and sub-surface sediments. For mineral-based amendments, remediation is generally accepted to occur by sequestration mechanisms: surface adsorption and structural incorporation, both of which may have several dynamic molecular scale variations [3]. Contamination by most heavy metals assumes significant environmental concern in acid soils (pH < 6.5) where the migration of metals will largely depend on soil organic matter content, redox potential and pH. Therefore organic wastes could play key roles in remediation and restoration of metal- contaminated soil by i) binding metals directly on their negatively charged surfaces, thus making metals less susceptible to leaching and bioavailability to plant and soil biota [4], ii) increasing soil porosity thereby facilitating precipitation of metal oxyhydroxides; iii) increasing soil pH and inducing metal precipitation; iv) enhancing soil quality by improving its structure, reducing nutrient imbalance and increasing microbial growth which in turn promotes the re-establishment of soil's natural ecological cycles, etc. Thus while organic matter may not remove toxic heavy metals from the soil, it can contribute to stabilizing and immobilizing them. Several published works on the use of organic wastes to remediate organic pollutants in soil have reported favourable results [5, 6]. Organic wastes contain microorganisms which can promote the breakdown of simple and complex organic pollutants [7, 8] and establish functionally diverse microbial community in the soil. Indirectly, organic wastes in contaminated soil can stimulate plant growth and the uptake, decontamination and gaseous loss of organic pollutants [9, 10].

The use of mixtures of organic and mineral (inorganic) materials as amendments for remediation of contaminated soil has not been widely reported. In this communication admixtures of poultry manure and termitaria (termite mound soil) were evaluated as amendment for remediation of heavy metals and petroleum hydrocarbons in contaminated soil. In previous communications [11-14] we reported on the use of poultry manure, cow dung, piggery waste in remediation of soil contaminated with petroleum hydrocarbons and for immobilization of heavy metals in contaminated soil. Termitaria are built of earth particles cemented together forming hard, brick-like, difficult to pick materials that are resistant to weathering. Its geochemical composition makes it a candidate amendment material for immobilization of heavy metals in soil [15]. It was thought that scrupulous admixture of poultry manure and termitaria may combine the surface chemical characteristics of the latter and nutrient-rich composition of poultry manure to enhance remediation of contaminated soil.

Materials and Methods

Top soil samples were collected using randomized quadrant method from the vicinity of automobile workshop and adjacent abandoned petroleum products station in Evboneka, Benin with the aid of soil auger. The soil samples were air-dried, sieved through a 2mm mesh and equal amounts of the samples were mixed thoroughly to obtain representative contaminated soil sample. Poultry manure was collected from a livestock farm in Evboneka, air-dried, ground and sieved through 200 μm mesh. Termite mound soil samples were collected from termitaria in the plantation of the Nigerian Institute of Oil Palm Research, Evboneka, Benin. Aggregate sample from ten different termite mounds was air-dried and sieved and sieved through 200 μm screen. The materials; soil, poultry manure and termite mound soil samples were characterized in terms of physico-chemical properties, selected heavy metals and total petroleum hydrocarbons content (Table 1).

The amendment materials; poultry manure and termite mound soil, were mixed in various proportions to contain 0, 20, 50, 80, 90 and 100 wt% poultry manure, slurried in deionized water, formed into 2mm pellets and air-dried.

Determination of water extractable and bioavailable metal fractions in the test soil samples

The pelletized amendment materials were applied to the contaminated soil at constant rate (11.11 wt% soil) re-wetted to 60% of the water retention capacity of the soil and kept at ambient temperature. The water extractable and bioavailable metal fractions in the unamended and amended soil samples were determined after various durations of amendment application (0, 30, 60, 90, 120 days) using the methods described by [16, 17] respectively. The effect of the level of the pelletized amendment application (0, 0.5, 2.0, 4.0, 8.0, 10 and 15 wt% contaminated soil) on the water extractable and bioavailable metal fractions was similarly determined on the contaminated soil treated with amendment containing 50wt% poultry manure 60 days after amendment application. The sum of the water extractable and bioavailable heavy metals; arsenic, cadmium, chromium copper and lead, are reported as total levels of water extractable and bioavailable metal fractions in the contaminated soil samples.

Fate of petroleum hydrocarbons in test soil samples

The contaminated soil samples that were treated with amendment of different compositions were examined for residual total petroleum hydrocarbons content after various periods of time (30, 60, 90 and 120 days) of amendment application. The residual total petroleum hydrocarbons content was determined spectrophotometrically.

Plant uptake studies

Pot experiments using the method of Nolan *et al*. [18] with modifications [19] were used to assess the effect of amendment (of various composition) application on uptake and transferability of heavy metals by maize plant in the contaminated soil. Air-dried soil samples (1kg) were placed in plastic pots maintained at 60% field water capacity with deionized water. Four viable grains of maize were sown in each of the pots and left to germinate and grow under ambient conditions. Four weeks after planting, the maize shoots were cut 0.5cm above the ground. The roots and shoots were washed separately with deionized water, dried at 70^{o}C for 48 hr and ground. The ground samples were digested with HNO_3 (4:1 v/v) and the amounts of the heavy metals in the digestate were determined by AAS.

Effect of amendment application of enzyme activities in contaminated soil

Biochemical indices, enzyme activities were determined in amended and unamended soil samples as end-point indicators of remediation. β-glucosidase, urease, phosphatases, phosphomonoesterase and lipid peroxidase activities, to reflect a range of processes in decomposition, nutrient cycling and microbial activity were determined. β-glucosidase and phosphatase activities were measured spectrophotometrically using the methods described by Tabatabai and Bremner [20]. Urease activity was determined colorimetrically according to the method of Gianfreda *et al*. [21]. Phosphomonoesterase activity was determined following the method described by Saa *et al*. [22]. Lipid peroxidation was determined following the method described by Ifemeji *et al*. [23].

Results and Discussion

Physico-chemical properties and heavy metals content of soil, poultry manure and termite mound soil

The physico-chemical properties and selected heavy metals content of the soil, poultry manure and termite mound soil are given in Table 1.

Table 1: Physico-chemical properties and selected heavy metals content of contaminated soil, termite mound and poultry manure

Parameters	Soil	Termite mound soil	Poultry manure
pH	6.21±0.01	4.80±0.01	9.23±0.01
Organic matter (%)	5.78±0.077	1.62±0.08	4.42±0.28
P ($mg.kg^{-1}$)	8.17±0.130	4.42±0.11	0.14±0.02
N (%)	1.50±0.03	0.53±0.11	21.31±0.08
Organic carbon (%)	3.84±0.03	2.18±0.05	2.31±0.04
Ca ($meq.100g^{-1}$)	10.63±0.08	2.64±0.21	9.91±0.01
Mg ($meq.100g^{-1}$)	4.39±0.18	0.96±0.03	1.54±0.02
K ($meq.100g^{-1}$)	0.93±0.05	0.28±0.02	12.03±0.01
Na ($meq.100g^{-1}$)	0.54±0.04	0.17±0.02	1.13±0.02
CEC ($meq.100g^{-1}$)	16.49±0.35	4.05±0.24	24.51±0.06
Clay (%)	6.63±0.06	14.15±0.01	-
Silt (%)	2.63±0.12	1.85±0.02	-
Sand (%)	90.73±0.06	84.00±0.02	-
As ($mg.kg^{-1}$)	8.00±0.36	0.22±0.02	0.05±0.03
Cu ($mg.kg^{-1}$)	43.43±0.09	5.25±0.03	4.93±0.02
Pb ($mg.kg^{-1}$)	25.43±0.85	0.32±0.02	0.04±0.02
Cd ($mg.kg^{-1}$)	10.83±0.32	0.11±0.01	0.03±0.01
Cr ($mg.kg^{-1}$)	20.90±0.56	0.09±0.01	0.03±0.01

The total heavy metals content of the contaminated soil was found to be 110.69±3.08 $mg.kg^{-1}$; made up of As 8.00±0.36 $mg.kg^{-1}$; Cd 10.83±0.33 $mg.kg^{-1}$; Cr 20.90±0.56 $mg.kg^{-1}$; Cu 43.43±0.99 $mg.kg^{-1}$ and Pb 25.45±0.85 $mg.kg^{-1}$ and gave values of degree of contamination, CD, and pollution load index, PLI of 77.46 and 13.92 respectively and indicate that the soil is severely contaminated with respect to the heavy metals. The total petroleum hydrocarbons content (THC) of the contaminated soil was 208.30±0.62 $mg.kg^{-1}$, which when compared with the level in control soil sample, 0.08±0.01 $mg.kg^{-1}$, indicates marked elevation of THC in the contaminated soil. Single extraction of the contaminated soil sample with deionized water and 0.01M $CaCl_2$ solution gave total water extractable and bioavailable metal fractions of 9.62 $mg.kg^{-1}$ and 25.46 $mg.kg^{-1}$ respectively.

Textural analysis showed that the contaminated and termite mound soil samples contained large proportions of sand (90.73±0.06% and 84.00±0.02%), followed by clay (6.63±0.06% and 14.15±0.01%) and silt (2.63±0.12% and 1.85±0.02%) respectively, classifying both materials as sandy loam. Soil texture influences properties of soil such as porosity, ease of aeration, nutrient status and available and thus affect the treatability of contaminated soil via immobilization technique. The pH of the materials varied from 4.80±0.01 for termite mound soil, through 6.21±0.01for contaminated soil and 9.23±0.01 for poultry manure. pH is important in many soil dynamic chemical interactions [24] particularly adsorption, complexation and release of metals. Cation exchange capacity measures the capacity of soil to allow for exchange (retention) of cations between its surface and soil solution and varied from 4.05±0.24 meq.100g^{-1} in contaminated soil to 24.51±0.06 meq.100g^{-1} in poultry manure. These results suggest that termite mound soil may produce a material that would be useful for the remediation of contaminated soil.

Effect of amendment application on water extractable and bioavailable metal fractions in the contaminated soil

The results of the observed effects of composition and duration of amendment application on the total levels of water extractable and bioavailable metal fractions in the contaminated soil are given in Table 2.

Table 2: Levels of total water extractable and bioavailable heavy metals in contaminated soil treated with poultry manure/termite mound soil amendment

Composition of amendment (wt% poultry manure)	Total water extractable metal fraction (mg.kg^{-1})			
	Duration of amendment application (Day)			
	30	60	90	120
0	7.61±0.19 (21.41±4.0)	6.53±0.19 (18.37±0.29)	4.06±0.14 (17.03±0.22)	1.35±0.07 (7.57±0.33)
20	7.60±0.42 21.56±0.39	6.14±0.20 (18.56±023)	3.66±0.25 (14.44±0.35)	1.11±0.06 (6.91±0.29)
50	7.60±0.26 (20.97±0.36)	5.88±0.20 (18.66±0.40)	3.34±0.27 (13.56±0.40)	1.03±0.06 (7.70±0.56)
80	7.07±0.27 (20.94±0.45)	5.30±0.31 (17.40±0.35)	3.31±0.10 (14.23±0.33)	1.07±0.21 (5.57±0.33)
90	7.37±0.36 (19.89±0.50)	5.13±0.24 (16.26±0.28)	3.46±0.31 (12.13±0.19)	0.97±0.16 (5.53±0.36)
100	8.02±0.38 (21.73±0.31)	6.33±0.31 (19.03±0.03)	4.74±0.24 (15.30±0.36)	1.89±0.19 (8.97±0.47)

Total levels of bioavailable metal fraction in parentheses

The results show marked reductions in total water extractable and bioavailable metal fractions in the contaminated soil following poultry manure/termite mound soil amendment application in comparison with unamended soil sample for the corresponding levels were 9.63 mg.kg^{-1} and 25.46 mg.kg^{-1} respectively. Close examination of the results in Table 2 reveals that the variation in the relative reduction in bioavailable metals fraction in the contaminated soil is both composition and duration of amendment application dependent. Reductions in levels of bioavailable metal fraction was generally highest for the longest duration of amendment application (120 days) used in this study and varied from 64.77% for amendment composition of 100 wt% poultry manure, 70.16% for amendment composition of 100 wt% termite mound soil as 89.92% for amendment with 90 wt% poultry manure. These results suggest apparent synergism in heavy metal sequestration by mixtures of poultry manure and termite mound soil, particularly amendment material with high (> 50 wt%) poultry manure content. The mechanism by which poultry manure combine with termite mount soil to enhance heavy metals binding capacity is not fully understood. Termite mound soil is a mineral-based material which can bind heavy metals by surface adsorption onto oxide and silicate minerals to form strongly bound inner-sphere complexes. Biosolids on account of their high pH, cation exchange capacity, organic matter and mineral nutrient content can act to reduce heavy metal mobilization in soil [4]. Chemical alteration of soil heavy metals to less soluble and bioavailable forms correspond to pollution abatement/amelioration, an index of soil remediation.

The effect of various levels of amendment (containing 50 wt% poultry manure) on the levels of water extractable and bioavailable metal fractions is given in Table 3. The variations of total water extractable and bioavailable metal fraction with level of amendment containing 50 wt% poultry manure application is shown in Fig. 1. These results show that poultry manure/termite mound soil amendment is effective even at low levels in immobilizing heavy metals in the contaminated soil even at relatively low level of amendment application. It can

Table 3: Levels of water-extractible and bioavailable metal fractions in contaminated soil amended with poultry manure-termite mound soil pellets

Level of amendment application (%)	Water-extractable metal fractions (mg.kg^{-1})				
	As	**Cu**	**Pb**	**Cd**	**Cr**
0	0.74±0.01 (1.54±0.03)	2.59±0.02 (7.51±0.02)	2.02±0.01 (5.02±0.02)	0.97±0.02 (3.82±0.01)	1.54±0.01 (4.99±0.03)
0.5	0.71±0.01 (1.52±0.01)	2.54±0.02 (7.43±0.02)	1.99±0.02 (4.87±0.04)	0.96±0.01 (3.29±0.02)	1.48±0.01 (4.90±0.01)
2.0	0.65±0.02 (1.44±0.02)	2.46±0.04 (7.36±0.03)	1.91±0.04 (4.76±0.01)	0.94±0.03 (3.73±0.02)	1.44±0.03 (4.74±0.04)
4.0	0.60±0.03 (1.36±0.02)	2.35±0.02 (7.19±0.05)	1.84±0.03 (4.67±0.03)	0.82±0.01 (3.45±0.04)	1.34±0.02 (4.53±0.02)
8.0	0.53±0.03 (1.24±0.03)	2.27±0.02 (7.03±0.02)	1.66±0.04 (4.41±0.01)	0.76±0.02 (3.27±0.03)	1.21±0.02 (4.15±0.02)
10.0	0.47±0.02 (1.07±0.02)	2.18±0.03 (6.80±0.04)	1.53±0.03 (3.85±0.02)	0.73±0.02 (3.04±0.03)	1.06±0.03 (3.97±0.03)
15.0	0.48±0.01 (1.02±0.03)	2.16±0.01 (6.75±0.04)	1.54±0.01 (3.70±0.03)	0.72±0.01 (2.96±0.02)	1.01±0.01 (3.91±0.02)

Levels of bioavailable metal fraction in parentheses

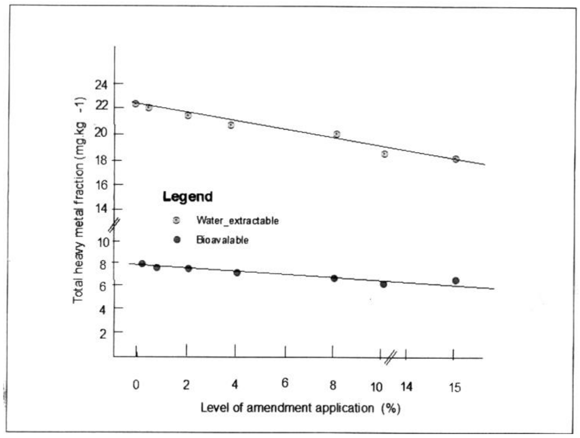

Fig. 1: Variation of total levels of water-extractable and bioavailable metals with level of amendment application

be seen from the results that a 30-fold increase in the level of amendment application was associated with less 25% (23.63 % with respect to water extractable and 18.56% bioavailable metal fractions) reduction in available metal fractions. The suggestion is that application of relatively low levels of about 5 wt% of the amendment may produce optimum reduction levels of available metal fractions in the contaminated soil.

Effect of amendment application on degradation of petroleum hydrocarbons

The variations of residual total petroleum hydrocarbons with composition and duration of amendment applications are given in Table 4.

The results show a decrease in the residual levels of petroleum hydrocarbons in the contaminated soil with composition and duration of amendment application. For the duration of apparent minimum residual petroleum hydrocarbons (120 days) a near quantitative degradation (95%) of petroleum hydrocarbons was reported for amendment with 100 wt% poultry manure. Fig. 2 shows effectiveness of degradation of petroleum hydrocarbons of single amendment (poultry manure and termite mound soil) application to the contaminated soil in comparison with unamended (control) soil.

The physico-chemical properties and constituents of the poultry manure component of the amendment that would be implicated in enhancing petroleum hydrocarbons degradation, and to various extents, are pH, cation exchange capacity, organic matter, phosphorus and nitrogen.

Table 4: Effect of poultry manure/termite mound amendment application on residual total petroleum hydrocarbons in contaminated soil

Composition of amendment (wt%) poultry manure)	Duration of amendment application (Days)			
	30	60	90	120
0	158.43±0.40	158.13±0.92	149.30±0.90	138.27±0.37
20	157.83±0.33	98.57±0.59	57.63±0.54	13.83±0.25
50	157.30±0.67	95.57±0.94	55.80±0.65	12.87±0.31
80	162.97±0.57	92.13±1.11	52.73±1.50	11.80±0.64
90	166.10±0.96	91.33±0.43	51.90±0.62	11.63±0.35
100	151.53±0.51	93.80±0.78	53.50±0.79	8.93±0.46
Control (Unamended)	196.60±0.51	193.30±0.52	191.27±0.74	183.07±0.94

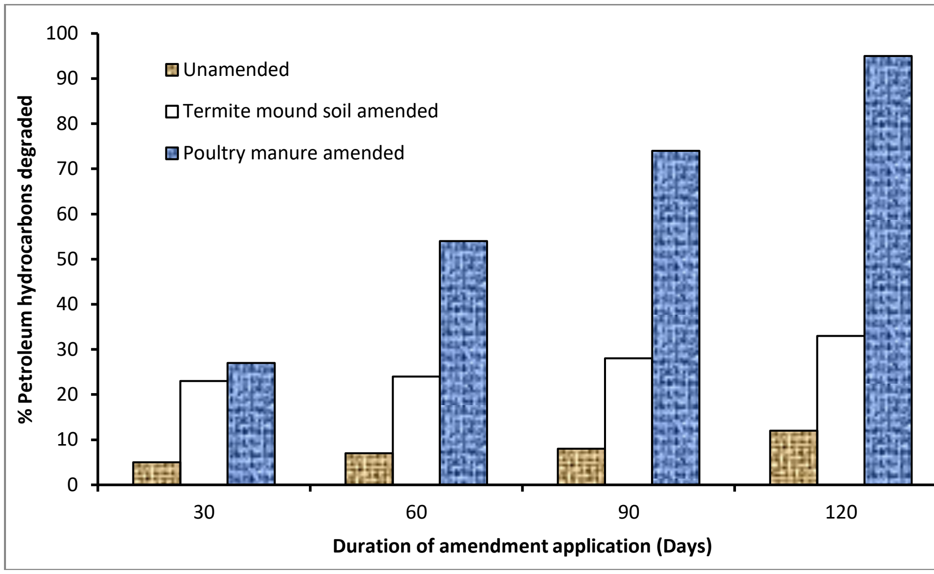

Fig. 2: Effect of poultry manure/termite mound application on degradation of petroleum hydrocarbons in contaminated soil

Addition of nutrients in bioremediation of contaminated soil biostimulates endogenous microflora to degrade xenobiotics However interaction with termite mound soil (with low pH) and active oxide surface may alter the availability of the nutrient component of poultry manure and mitigate the effect of the latter on biodegradation. This effect will be expected to be greater at lower poultry manure-to-termite mound soil component of the amendment and would explain the trend of the results obtained in this study.

Effect of amendment application on metal uptake by maize (*Zea mays* L.) plant

Table 5 gives the effect of amendment composition on the uptake of heavy metals in the contaminated soil. Sequestration of contaminants in soil following amendment application should be associated with reduced bioavailable contaminants for plant uptake in comparison with unamended (control soil), the results in Table 5 show marked reductions of 18-fold and 25-fold in total heavy metals uptake by roots of maize plant and translocation to maize shoots respectively following poultry manure/termite mound soil amendment application. Reductions in bioavailable metal fractions and in metal transferability will ameliorate metal phytotoxicity and accentuate re-vegetation of contaminated site, an important remediation end-point. The metal transfer coefficient, based on total bioavailable metal fractions in the soil and translocation factor are shown in Fig. 3 as function of amendment composition. The process involved in plant uptake of heavy metals in soil include (i) transport of metals in solution to roots by diffusion and mass flux; (ii) adsorption and uptake by roots; (iii) transfer to xylem and translocation to

Table 5: Effect of poultry manure/termite mound soil amendment application on total heavy metals uptake by maize plant in contaminated soil. Duration of amendment application 120 days

Composition of amendment	Total levels of heavy metals (mg.kg^{-1})			
(wt% poultry manure)	Roots	TC	Shoots	TF
0	0.34±0.002	82	0.28±0.01	1.2
20	0.28±0.01	61	0.17±0.02	1.6
50	0.42±0.02	40	0.17±0.01	2.5
80	0.27±0.02	59	0.16±0.01	1.6
90	0.23±0.01	48	0.11±0.01	2.1
100	0.39±0.03	54	0.21±0.02	1.9
Unamended (Control)	4.42±0.41	64	2.85±0.18	1.55

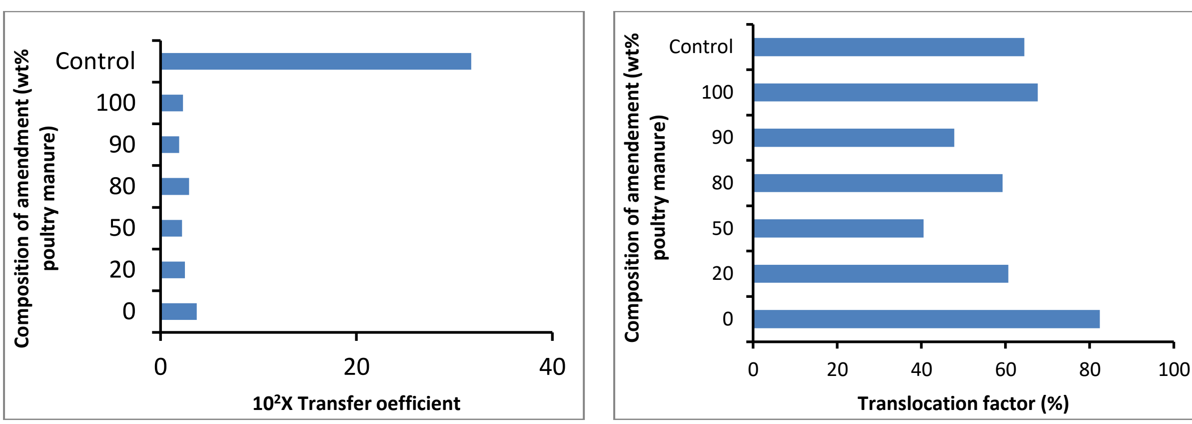

Fig. 3: Heavy metals transfer coefficient (A) and translocation factor (B) in contaminated soil treated with poultry manure/termite mound soil amendment

shoots [25]. The amount of heavy metals in soil solution is an important limiting factor that affect their plant. The observed marked reductions in metals uptake by maize plant following poultry manure/termite mound soil application can be associated with reductions in bioavailable metal fraction in the contaminated soil.

The result (Table 5) show that large proportions of the metals in maize roots (up to 82%) was translocated to the shoots with values of translocation factor in the range of 0.40 to 0.82 and are consistent with the suggestion that maize plant is not metal hyperaccumulating and may be described as excluder [26]. The transport of metals from roots to shoots involves long distance translocation in the xylem and storage in the vacuole of leaf cells; processes that are affected by concentration of available metal in soil, solubility sequences in the shoots and nature of plant species [27].

Effect of amendment application on enzyme activities in contaminated soil

The variations of enzyme activities in the contaminated soil with the composition of the amendment are shown in Figs. 4 and 5. The results show increase in enzyme activity in apparent dependence on the poultry manure content of the amendment, with the application of 100 wt% poultry manure giving the highest activity of all enzymes studied. The dependence of enzyme activity on the poultry manure content of the amendment may be ascribed to the relatively higher organic carbon content of poultry manure (21.31±0.40 %)

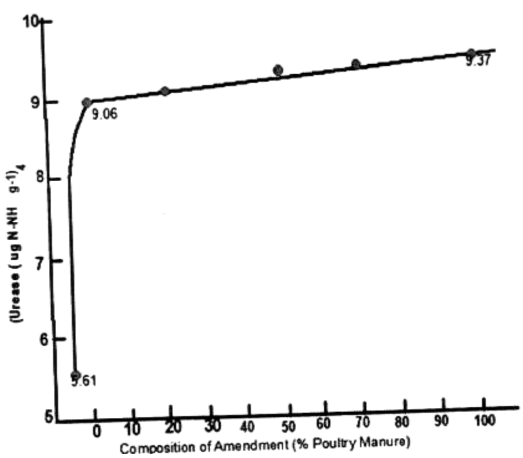

Fig. 4: Effect of termite mound soil/poultry manure application on activity of urease in soil co-contaminated with heavy metals and petroleum hydrocarbons

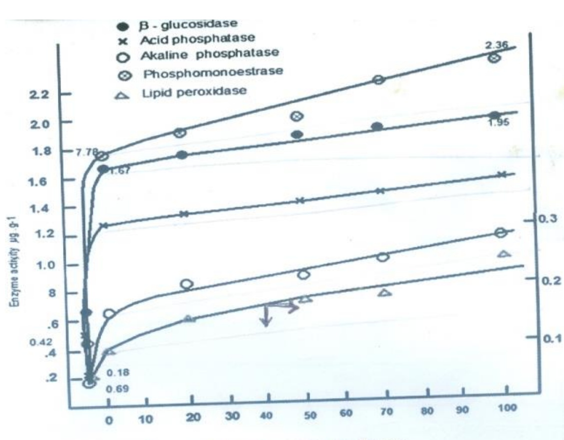

Fig. 5: Effect of termite mound soil/poultry manure application on activity of enzyme in soil co-contaminated with heavy metal and petroleum hydrocarbons

than in the termite mound soil (2.18±0.05 %). It is generally well known that enzymes are sensitive to any soil organic matter content, in comparison with unamended soil maximum increase in soil activity ranged from 67.02% for urease to 522.22% for alkaline phosphate; while with respect to amendment composition, increase in enzyme activity was less marked and varied from 3.42% for urease to 58.33% for lipid peroxidase (Table 6).

Table 6: Recovery of enzyme activity in co-contaminated soil following application of poultry manure/termite mound soil

Enzyme	Increase in enzyme activity (%)
Urease	67.02[a] (3.42)
β-glucosidase	183.61[a] (15.77)
Phosphomonosterase	402.15 [a] (32.58)
Acid phosphatase	190.74 [a] (21.87)
Alkaline phosphatase	522.22 [a] (45.45)
Lipid peroxidase	300.00 [a] (58.33)

[a]In comparison with unamended soil; values in parenthesis compare activity in soil amended with 100% poultry manure and 100% termite mound soil

This apparent increase in enzyme activity following the application of poultry manure/termite mound soil pellets to the contaminated soil is considered to be consequent on immobilization of heavy metals and degradation of petroleum hydrocarbons in the soil. It is to be noted that at the level of maximum enzyme activity, the total available heavy metals and total petroleum hydrocarbons contents of the treated soil were 10.01 mg.kg^{-1} and 8.93 mg.kg^{-1} respectively, and are several orders of magnitude lower; about 20-fold in respect of heavy metals and 23-fold in respect of total petroleum hydrocarbons than in untreated soil sample. Fig, 6 provides a comparison of enzyme activities in the untreated contaminated soil, contaminated soil amended with biochar (100%) and poultry manure (100%); to clearly indicate the effectiveness of amendment application in restoring soil quality.

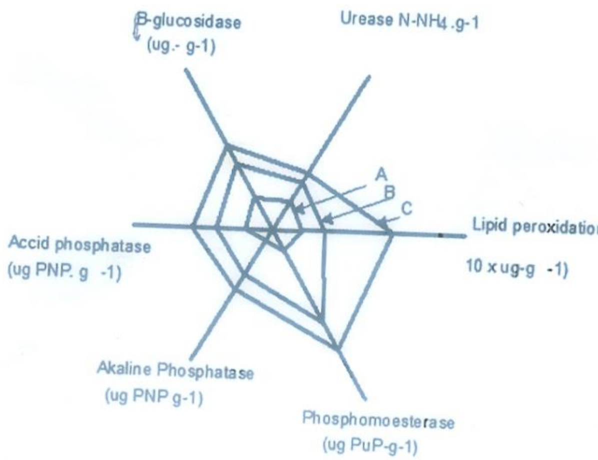

Fig. 6: Comparison of activities of enzymes in co-contaminated soil, (A) untreated soil (B) treated with termite mound soil, and (C) treated with poultry manure

These results show that quality of the contaminated soil, measured in terms of enzyme activities was enhanced following the application of amendment: with the treatment with poultry manure (100%) showing marked enhancement in soil quality in comparison with treatment with termite mound soil. There was no apparent synergistic effect of the amendments on the measured enzyme activities suggesting that the pathway of contaminant mitigation by poultry manure and termite mound soil may be different and perhaps independent.

Conclusion
The application of reactive or stabilizing materials for remediation of heavy metal and organic contaminants in soils and sediments is a generally well accepted technology to ameliorate their deleterious environmental and/or public health impact. This report demonstrated the relative effectiveness of admixtures of poultry manure and termite mound soil to sequester/degrade/stabilize heavy metal and petroleum hydrocarbons contaminants in co-contaminated soil. Optimization of composition, level and duration of poultry manure/termite mound soil amendment application for contaminant remediation in soils and sediments is the necessary next step of these studies.

References
1. P.A. O'Day and D. Viassopoulos, Mineral-based amendments for remediation. *Elements*, **6**: 375-381 (2010).
2. D.L. Jones and J.R. Healey, Organic amendments for remediation: Putting waste to good use. *Elements*, **6**: 369-374 (2010).
3. N. Bolan, R. Naidu, G. Choppala, J. Park, M.I. Mora, D. Budianta and P. Panneercelcvan, Solute interactions in soil in relation to the bioavailability and environmental remediation of metals metalloids. *Pedologist*, **2(1)**: 1-18 (2010).
4. M. Farrel and D.I. Jones, Use of compost in the remediation of heavy metal contaminated soil. *J. Hazard Mater*., **175**: 575-582 (2010).
5. M.A. Cole, I. Zhang and Liu, X. Remediation of pesticide contaminated soil by planting and compost addition. *Compost Science & Utilization*, **3**: 20-30 (1995).
6. Z.A. Hickman and B.J. Reid, Increased microbial catalytic activity in diesel contaminated soil following addition of earthworms (*Dendrovaana veneda*) and compost. *Soil Biol. Biochem*., **40**: 2920-2926 (2008).

7. K.T. Semple, B.J. Reid and T.R. Fermor, impact of composting strategies on the treatment of soils contaminated with organic pollutants. *Environ. Pollut*., **112**: 267-283 (2001).
8. B. Antizar-Ladislao, Bioremediation: Working with bacteria. *Elements*, **6**: 389-394 (2010).
9. F.M.G. Tack and E. Meers, Assisted phytoextraction: Helping plants to help us. *Elements*, **6**: 383-388 (2010).
10. I. Kuiper, E.L. Lagendijk, G.V. Bloemberg and B.I.J. Lutenberg, Rhizo-remediation: A beneficial plant-microbe interaction. *Mol. Plant Microbe Interact*., **17**: 6-5 (2004).
11. I.O. Ogu and F.E. Okieimen, Note on the effect of piggery waste application on the biodegradation of petroleum hydrocarbons in soil. *Niger. J. Appl. Sci*., **26**: 181-183 (2008).
12. C.O. Okieimen, and F.E. Okieimen, Bioremediation of crude oil polluted soil. Effect of poultry droppings and natural rubber processing sludge application on the degradation of petroleum hydrocarbons. *Environ. Sci*., **12**: 1-8 (2005).
13. D.O. Emwanta and F.E. Okieimen, Immobilization and phytoavailability of As, Cr and Cu in CCA contaminated soil. Effect of poultry manure application. *Niger. J. Chem. Res*., **15**: 1-11 (2010).
14. D.E. Ogbeifun, L.B. Okenwa, F.E. Okieimen and E.G. Uwumarongie, Capacity of termitaria in reducing bioavailability of As, Cr and Cu in chromated-copper-arsenate (CCA) contaminated soil. *J. Chem. Soc. Niger*., **36(1)**: 29-36 (2011).
15. C.O. Anoduadi, L.B. Okenwa, F.E. Okieimen, A.T. Tyowua and E.G. Uwumarongie-Ilori, Metal immobilization in CCA contaminated soil using laterite and termite mound soil. Evaluation by chemical fractionation. *Niger. J. Appl. Sci*., **27**: 77-87 (2009).
16. G.O. Tsetimi and F.E. Okieimen Chelate-assisted phytoextraction of heavy metals from CCA contaminated soil. *J. Environ. Chem. Toxicol*., **3(8)**: 214-224 (2011).
17. D.P. Oliver, K.G. Tiller, A.M. Alston, R. Naidu and G.D. Cozens A comparison of three soil tests for assessing Cd accumulation in wheat grain. *Aust. J. Soil Res*., **37**: 1123-1138 (1999).
18. A.L. Nolan, H. Zhang and M.J. McLaughlin, Prediction of zinc, cadmium, lead and copper availability to wheat in contaminated soil using chemical speciation, diffuse gradient in thin films, extraction and isotopic dilution techniques. *J. Environ. Qual*., **34**: 496-507 (2005).
19. A. Battaglia, N. Calace, R. Naidu, B.M. Petronoi and M. Pietroletti, Reduction of Pb and Zn bioavailable forms of metal in polluted soil due to paper mill sludge addition. Effects of Pb and Zn transferability to barley. *Bioresource Technol*., **98(16)**: 2993-2999 (2006).
20. M.A. Tabatabai and J.M. Bremner, Use of ρ-nitrophenyl phosphate for assay of soil phosphate activity. *Soil Biol. Biochem*., **1**: 301-307(1969).
21. I. Gianfreda, E. Sannimo, N. Orteta and P. Nannipieri, Activity of free and immobilized urease in soil: Effect of

pesticides. *Soil Biol. Biochem*., **26**: 777-784 (1994).

22. A. Saa, M.C. Trasar-Cepeda, F. Gil-Stores and T. Carballas, Changes in soil Phosphates and phosphatase activity immediately following forest fires. *Soil Biol. Biochem*., **25**: 1223-1230 (1993).
23. S.C. Ifemeji, A.U. Uchedi, A.C. Okechukwu, C.B. Nwaka, I.N. Lekong, C. Anene and I.C. Ezeude, Determination of total protein superoxide dismutase, catalytic activity and lipid peroxidation in soil micro-fauna (earthworm) from Onitsha municipal open waste dump. *J. Sci. Res. Repts*., **6(5)**: 394-403(2015).
24. S. Tokalioglu, S. Kartal and A. Guttekin, Investigation of heavy metal uptake by vegetables growing in contaminated soil using the modified BCR sequential extraction method. *Intern. J. Environ. Anal. Chem*., **88(6)**: 417-430 (2006).
25. S.K. Wenger, S.K. Gupta and R. Schulin, The role of nitrile triacetate in chelate-assisted phytoremediation. *Dev. Soil Sci*., **32**: 679-695 (2008).
26. R.A. Wuana and F.E. Okieimen, Phytoremediation potential of maize (*Zea mays* L.) plant. A review. *Afr. J. Gen. Agric*., **6(4)**: 275-287 (2010).
27. X.E. Yang, V.C., Baligar, J.C. Foster and D.C. Martens, Accumulation and transport of nickel in relation to organic acids in rye grass and maize growth with different nickel levels. *Plant Soil*, **197**: 271-276 (1997).