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Phytoremediation Potentials of Selected Plants in Crude Oil-Polluted Soils

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Abstract

Phytoextraction involves the absorption of contaminants by roots followed by translocation and accumulation in the aerial parts. It is mainly applied to metals (Cd, Ni, Cu, Zn, Pb) but can also be used for other elements (Se, As) and organic compounds. Experiments were carried out with 24 polyethylene pots each containing 7 kg of sandy loam soil mixed with 50 ml of crude oil. Twelve containers contained the crude oil-polluted soil while the remaining twelve containers contained the Control soil. Seeds of *Amaranthus hybridus* L., *Tithonia diversifolia, Abelmoschus esculentus* L. and *Zea mays* were sown in polyethylene containers containing 7 kg of contaminated or Control soil. The seeds were sown after two weeks of spiking the soil with crude oil. After two months, plants were harvested, separated into roots and shoots. Five heavy metals, namely Copper, Lead, Chromium, Cadmium and Nickel were evaluated. On the basis of the results obtained, the plants were classified as accumulators, hyperaccumulators, indicators or excluders. The results showed that *Z. mays* has the ability to accumulate Cu, stabilize Pb and Ni in crude oil-polluted soils. *Z. mays* is an excluder of Cr and Cd in crude oil-polluted soil. *Z. mays* showed suitability for Cr accumulation in Control soil with TF > 1 but less suitable for Pb extraction in Control soil with BCF, TF and BAF < 1. *A. esculentus* is suitable for phytoextraction of Cu, Cr and Pb, phytostablize Ni and Cd in Control soil. *A. esculentus* proved suitable for Cd phytoextraction in crude oil-polluted soil but less suitable for Ni extraction in crude oil-polluted soil. *A. hybridus* is an accumulator of Cu, Cd and Pb, stabilizer of Cr and Ni of crude oil-polluted and an excluder for Cr and Ni for Control soil. *T. diversifolia* was the most efficient in remediating Cu and Cd in crude oil-polluted soil. *A. esculentus* had the highest remediation factor in both crude oil-polluted (0.0475%) and Control soil (0.048%). *A. esculentus* was the most efficient at remediating Cd in crude oil-polluted soil, while *T. diversifolia* was the most efficient in the remediation of Cd in Control soil.

Keywords: Crude oil, heavy metals, phytoextraction, phytoremediation, accumulators.

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Introduction

Soil pollution with oil spills is a major global concern currently (Bijay *et al*., 2012). Soil pollution with crude oil has severe health risks, causes pollution of ground water, financial loss and, ecological problems, and reduces the agricultural productivity of the soil (Odu, 1977). The toxicity of crude oil to microorganisms, plants, animals and humans is well established (Bijay *et al.*, 2012). The causes of crude oil pollution of the soil are spills from crude oil installations, accidents during conveyance and oil bunkering. Crude oil-polluted soil puts some limitations on soil health which includes low nutrient, reduced soil moisture, erosion, low pH, low soil organic matter, reduced soil aeration, loss of soil biodiversity. Restoration of crude oil-polluted site by physical or physicochemical (e.g., soil washing, vapour extraction, thermal desorption) processes is expensive and not ecologically friendly and they are frequently used as first steps in the removal of the crude oil (Bijay *et al.*, 2012). A comprehensive cleanup of crude oil spills can be attained through phytoremediation.

Soils from oil-contaminated sites could also be contaminated with metals, salts, and/or pesticides, thus complicating phytoremediation efforts. Cunningham *et al.* (1996) found that sodium salts as well as a variety of heavy metals (e.g. Cr, Pb, Hg, Zn, Ni, Cu, and Cd) are commonly encountered on sites contaminated with organic pollutants. Little information exists on the effect of mixtures of these contaminants on phytoremediation efforts.

The term phytoextraction concerns the removal of heavy metals from the soil by means of plant uptake. This technology is based on the ability of the roots to absorb, translocate and concentrate heavy metals from soil to the above-ground harvestable part of the plant. The process results in a reduction of the polluted mass and also in the removal of the metal from an aluminosilicate based matrix (soil) to a carbon based matrix (plants) (Blaylock and Huang, 2000).

The identification of heavy metal hyperaccumulators, that is, plants capable of accumulating extraordinarily high metal levels, reveals that plants have the genetic potential to clean up polluted soil (Nadia *et al.,* 2012). Accumulators are also characterized by a shoot-to-root metal concentration ratio (the translocation factor (TF) of > 1, whereas, non-hyperaccumulator plants species usually have high metal concentrations in the roots than in the shoots. Several researchers e.g. Sun *et al.* (2008) include the bioaccumulation factor (BAF) as an element for classification as an accumulator species. The BAF refers to the plant metal concentration in root and the soil metal concentration ratio. This ratio should be > 1 for inclusion into the hyperaccumulator group. The importance of hyperaccumulators has stimulated the emphasized on further research in exploring the polluted sites and discovering new hyperaccumulator plants. Many plant have become metal tolerant due to the adaption of plant species to heavy metals, as these plant species have been growing in the polluted soils for a long period (Nadia *et al.*, 2012). The aim of this study was to determine the potentials of the selected plants for phytoextraction of heavy metals from hydrocarbon-polluted soil.

Materials and Methods

Study site

The experiments were carried out in the Botanical Garden of the University of Ilorin, which is located in Ilorin, Kwara State. The Botanical Garden of University of Ilorin is located in the Southern Guinea savanna zone of Kwara State, Nigeria. The area falls within latitudes $8^0$27.810’ N and $8^0$28.230’ N and longitudes $4^0$38.920’ E and $4^0$39.971’E. The site is characterized by a monomodal rainfall pattern. The rainy season is from April to October with a dry spell in late June and fairly rainfall in August. The temperature of the wet months ranges between 24 ºC and 27 ºC while in dry months it ranges between 29 ºC and 35ºC.

Uptake of heavy metals by selected plants

The method of Ogunkunle *et al.* (2013) was adopted. The experiment was carried out in the Botanical garden of the University of Ilorin, Nigeria, with 24 polyethylene pots each containing 7 kg of sandy loam soil mixed with 50 ml of crude oil. The crude oil (Brass blend) was collected from Midwestern oil and gas company Ltd, Lagos. Twelve containers contained the crude oil-polluted soil while the remaining twelve containers contained the Control soil. Seeds of *Amaranthus hybridus* L., *Tithonia* *diversifolia, Abelmoschus esculentus* L. and *Zea mays* were sown in polyethylene containers containing 7 kg of contaminated or Control soil.

The seeds were sown after two weeks of spiking the soil with crude oil. Six containers per treatment were used for each plant species. The containers were arranged in a complete randomized design (CRD). Two weeks after planting, plants were thinned to four seedlings per container. Plants were left to grow for two months with regular watering with borehole water under natural photoperiod and ambient conditions. After two months, plants were harvested, separated into roots and shoots, and washed with tap water to remove soil particles. Plant samples were properly labeled and oven-dried to constant weight at 80 °C.

Elemental analyses of soil and plant (root and shoot)

Analyses of the elemental contents of the soil, shoots and roots samples were determined with the adopted method of Abdulkadir *et al*. (2012). The air dried soil samples from each of the treatment were crushed, ground and powdered with a mortar and pestle. Each powdered soil sample (0.1 g) was carefully weighed into a test tube and a mixture of 0.5 ml Trioxo-nitrate V acid (HNO_3), 1.5 ml Perchloric acid ($HClO_4$) and 0.5 ml hydrofluoric acid (HF) were added to each sample. The content was heated on a hot plate in a fume cupboard till colourless solution was formed. After cooling, the residue were transferred into 50 ml beaker and made to volume up to 10 ml with deionized distilled water.

Similarly, the plant samples i.e., roots and shoots (stem and leaves) were crushed, ground and powdered separately with the help of a mortar and pestle. An amount of 0.1 g of each powdered plant sample was carefully weighed into a test tube and a mixture of 0.5 ml 70 % Perchloric acid ($HClO_4$), 2.5 ml Trioxo-nitrate (V) acid (HNO_3) and 0.5 ml Tetraoxo-sulphate (VI) acid (H_2SO_4) were added to each sample. The content was heated on a hot plate in a fume cupboard till the appearance of a clear solution. It was then set aside to cool. The residue was transferred into 50 ml beaker and made to the volume, up to 10 ml with deionized distilled water. The digested samples were then analyzed for their various heavy metals (Cr, Ni, Pb, Cu and Cd) by using Atomic Absorption Spectrophotometry (AAS).

Model for measuring potentials of the plants for phytoextraction

Biological Concentration Factor (BCF) and Translocation Factor (TF)

Biological Concentration Factor (BCF) was calculated as metal concentration ratio of plant roots to soil given in equation I (Ginocchio and Baker, 2004). Translocation Factor (TF) is described as ratio of heavy metals in plant shoot to that in plant root given in equation II (Li *et al.,* 2007). Biological Accumulation Coefficient (BAC) was calculated as ratio of heavy metal in shoots to that in soil given in equation III (Li *et al*., 2007). All these models were calculated for each of the four selected plants.

$$BCF = \frac{[Metals]_{root}}{[Metals]_{soil}}$$

$$TF = \frac{[Metals]_{shoot}}{[Metals]_{root}}$$

$$BAC = \frac{[Metals]_{shoot}}{[Metals]_{soil}}$$

Plant-Soil Relationships

Accumulation is manifested by species that accumulate greater metal concentrations in the aerial portions of the plant with shoot/root ratio (TF) > 1, BAC > 1 (Baker, 1981). Hyperaccumulation is manifested by species that accumulate higher concentrations of metals in aerial parts than found naturally in the soil. Indication: Levels of metals in the tissue are similar to those in the surrounding soil. Exclusion: Avoidance of metal uptake, metal restriction to the roots, shoot/root ratio (TF < 1) (Baker, 1981). Phytostabilization: Metal concentration ratio of plant roots to soil (BCF > 1), but shoot/root ratio (TF < 1).

Phytoextraction efficiency of the plants

This depends on the amount of heavy metals accumulated in the above-ground biomass of the plants and the plant yields. The remediation factor (RF) (Vyslouzilova *et al.,*

2003) which represents the percentage of an element removed by the plant dry above-ground biomass from the total content in the soil was calculated as follows:

$$RF = \frac{Pb_{plants} \times B_{plants}}{Pb_{soil} \times W_{soil}} \times 100$$

Where Pb_{plant} is the content of Pb in the plant dry above-ground biomass (mg kg-^{1}); B_{plant} is the plant above-ground biomass yield (g); Pb_{soil} is the total content of Pb in the soil (mg kg^{-1}) and W_{soil} the weight (g) of soil in the pot. This calculation was done for each of the heavy metals investigated.

Phytoextraction potential (PP)

This represents the total amount of heavy metals extracted per hectare of soil in one single phytoremediation cycle (Kos *et al*., 2003). It was calculated as follows:

$PP = Pb_{plant} \times B_{plant}$

Where Pb_{plant} is the content of Pb in plant dry above-ground biomass (mg kg-^{1}) and B_{plant} is the plant dry above-ground matter biomass yield (t ha-^{1}). This was calculated for all heavy metals investigated.

Biomass production

The biomass production of the plant materials was done by destructive sampling after two months of growth. The fresh and dry weights of the shoots and roots were measured and recorded.

Data Analyses

The data collected from the study were statistically analyzed with the use of SPSS 17. The means of the treatments were compared statistically with t-test and ANOVA. Graphs were plotted using Origin 7.0 software.

Results

Table 1 shows some physicochemical properties of the soil used for the study. The organic carbon and organic matter were 2.41% and 4.15% respectively. The pH (9.35) was basic. The Exchangeable base: Ca(16 Cmol^{-l}), Mg(19.08 Cmol^{-l}), Na(0.79 Cmol^{-l}) and K(0.22 Cmol^{-l}) were found. The concentrations of heavy metals of interest in mg/kg were Pb(625 mg/kg), Cd(125mg/kg), Ni(1062.5mg/kg), Cr(1250mg/kg) and Cu(20mg/kg). The exchangeable acid and effective Cation Exchange Capacity were 0.05 cmol^{-1} and 36.04 cmol^{-1}, respectively. The soil particle sizes were found to be sand, clay and silt and had 89.00%, 5.60% and 5.40% content respectively. Nitrate and phosphate concentration were 23.33% and 2.39%, respectively, while nitrogen and phosphorous were 0.54% and 95.00%, respectively.

Table 2 shows the BCF, TF and BAC of *Tithonia diversifolia* for Cu, Cr, Cd, Pb and Ni in both soils. The sequence of BCF for the metals in *Tithonia diversifolia* in crude oil-polluted soil was in this order: Cu >Pb> Cr > Ni > Cd and the sequence of BCF for the metals in Control soil was: Pb> Cu> Cd> Cr> Ni. The trend of TF for the metals in *Tithonia diversifolia* in crude oil-polluted soil was: Cd > Cr>Pb> Ni> Cu in Control soil. In the case of BAC, for crude oil – polluted soil, the trend was Cu >Pb> Cr >Ni > Cd while for Control soil, the order was: Pb> Cd > Cu > Cr > Ni. In crude oil-polluted soils, *Tithonia diversifolia* had BCF and BAC >1 for Cu, Cr and Pb while TF < 1 for Cu, Cd and Ni but greater than 1 for Cr and Pb. The BCF TF and BAC were <1 for Cr and Ni while the BCF and BAC were greater than 1 for Cu, Cd and Pb.

Furthermore, the BCF, TF and BAC for Pb in both soils were > 1 except for TF in Control soil which was < 1. Table 2 also shows that BCF, TF and BAC for Ni in the polluted soils were all < 1. These results showed that *Tithonia diversifolia*is suitable for the extraction of Cu and Pb in both soils, phytoextraction of Cr in crude oil-polluted soil and phytoextraction of Cd in Control soil but less suitable for the phytoextractrion of Cr in Control soil, less suitable for phytoextraction of Cd in crude oil-polluted soil and less suitable for phytoextraction of Ni in both soils. The results further showed the *T. diversifolia* is an accumulator of Cr and Pb but stabilizer of Cu in crude oil-polluted soil. It is also a phytostabilizer of Cu, Cd, Pb in Control soil (soil without crude oil).

Table 3 shows the heavy metal dynamics in *Zea mays* planted in crude oil-polluted and Control soils. The BCF of Cu, Cr, Cd, Pb and Ni in *Zea mays* in crude oil–polluted soil are recorded in this sequence: Cu >Pb = Ni > Cr > Cd; while in Control soil, the order is: Cd > Ni > Cu >Pb> Cr. The TF in the crude oil-polluted soil had the trend Cu >Pb> Cd > Cr > Ni, and Control had the trend: Cu > Cr >Pb> Ni > Cd. Biological accumulation coefficient (BAC) of the metals in *Zea mays* in crude oil-polluted soil shows that the sequence of extraction coefficient followed this other: Cu >Pb> Ni > Cd > Cr while in Control soil gave the order of BAC as: Pb> Cd > Cu > Cr > Ni. The BCF, TF and BAC of *Zea mays* for Cu in both soils were > 1 except that the BCF in Control soil was < 1. In the case of Cr, the BCF TF and BAC were < 1 but TF was > 1 in Control soil.

Table 4 shows the mobility of the selected metals in *Abelmoschus esculeutus* in both the Control and crude oil-polluted soils. In the crude oil-polluted soil, the sequence of BCF in *Abelmoschus esculentus* was: Cu > Pb> Cr > Ni > Cd, whereas, in Control soil, the order was Cd >Pb> Cu > Cu > Ni > Cr. At the same time, the TF of the metals in *Abelmoschus esculentus* was in this order in crude oil-polluted soil: Cd > Cr > Ni >Pb> Cu even as the TF in Control soil followed this order: Cr > Cu > Pb> Ni > Cd. In addition, the BAC for *Abelmoschus esculentus* for the metals in crude oil-polluted soil followed this order: Cr >Pb> Ni > Cu > Cd even as the BAC in Control soil also followed this order: Pb> Cu > Cr > Cd > Ni. *A .esculentus* had BCF, TF and BAC > 1 for Cu in Control soils. *A. esculentus* was able to accumulate Cr in both soils and acted as stabilizer for Pb in both soils and Cd in Control soil, but acted as excluder for other heavy metals.

Table 1: Baseline soil analysis

Sand	**Clay**	**Silt**	**Ca**	**Mg**	**Na**	**K**	**pH**	**H+Al**	**ECEC**	**Base Sat (%)**
89.00	5.60	5.40	16.00	19.08	0.79	0.22	9.35	0.05	36.04	99.99
Org. C (%)	**Org. M (%)**	**N (%)**	**PO_4 (%)**	**NO_3 (%)**	**P mg/kg**	**Pb mg/kg**	**Cd mg/kg**	**Ni mg/kg**	**Cr mg/kg**	**Cu mg/kg**
2.41	4.15	0.54	23.33	2.39	95.00	625	125	1062.5	1250	20

Table 2: Heavy metal dynamics in *Tithonia diversifolia* planted in crude oil-polluted and Control soils.

	Cu		**Cr**		**Cd**		**Pb**		**Ni**	
	CP	**Ctr**	**CP**	**Ctr**	**CP**	**Ctr**	**CP**	**Ctr**	**CP**	**Ctr**
BCF	7.17	1.63	1.54	0.63	0.08	1.35	2.68	1.65	0.80	0.53
TF	0.79	0.65	1.03	0.99	0.50	1.00	1.04	0.94	0.95	0.90
BAC	5.70	1.05	1.59	0.62	0.04	1.35	2.79	1.55	0.76	0.48

BCF: Biological Concentration Factor, TF: Translocation Factor, BAC: Biological Accumulation Coefficient, CP: Crude Oil-Polluted, Ctr: Control.

Table 3: Heavy metal dynamics in *Zea mays* planted in crude oil-polluted and Control soils.

	Cu		**Cr**		**Cd**		**Pb**		**Ni**	
	CP	**Ctr**	**CP**	**Ctr**	**CP**	**Ctr**	**CP**	**Ctr**	**CP**	**Ctr**
BCF	4.00	0.95	0.84	0.18	0.54	2.22	1.65	0.69	1.65	1.05
TF	1.33	1.33	0.85	1.25	0.86	0.33	0.96	0.93	0.74	0.91
BAC	5.33	1.27	0.71	0.22	0.46	0.72	1.60	0.64	1.22	0.96

BCF: Biological Concentration Factor, TF: Translocation Factor, BAC: Biological Accumulation Coefficient, CP: Crude Oil-Polluted, Ctr: Control.

Table 4: Heavy metal dynamics in *Abelmoschus esculentus* planted in crude oil-polluted and Control soils.

	Cu		Cr		Cd		Pb		Ni	
	CP	**Ctr**	**CP**	**Ctr**	**CP**	**Ctr**	**CP**	**Ctr**	**CP**	**Ctr**
BCF	1.54	1.44	0.92	0.71	0.03	2.35	1.47	2.15	0.76	1.32
TF	0.40	1.13	1.60	1.91	18.00	0.21	0.94	0.92	0.97	0.35
BAC	0.62	1.63	1.47	1.36	0.53	0.50	1.39	1.98	0.74	0.46

BCF: Biological Concentration Factor, TF: Translocation Factor, BAC: Biological Accumulation Coefficient, CP: Crude Oil-Polluted, Ctr: Control.

Table 5 reveals the metal dynamics in *Amaranthus hybridus*planted in both crude oil-polluted and Control soils. The trend of BCF of the heavy metals in *A. hybridus*for the selected heavy metals was: Cu > Cr >Ni >Pb> Cd in crude oil-polluted soil, while in Control soil the trend was: Pb> Cu > Cd > Ni > Cr. Furthermore, the TF in crude oil-polluted soil followed this order: Cu >Pb> Cd > Cr > Ni, but in Control soil, the order was: Cu > Cr >Pb> Ni > Cd. Also, the BAC in crude oil-polluted soil followed this order Cu >Pb> Cr > Ni > Cd while the BAC in natural-polluted soil followed this trend: Pb> Cu > Ni > Cd > Cr. *A. hybridus*had BCF, TF and BAC > 1 for Cu in both soils but had BCF, TF and BAC > 1 in Control soil for Cd and Pb. Table 6 further shows that Cd and Ni had BCF, TF and BAC < 1 in crude oil-polluted soils. The BCF and BAC for Ni in Control were > 1 while TF was < 1. On the other hand, BCF and BAC for Cd and Pb in crude oil-polluted soil were <1 while TF was > 1. In addition, the TF and BAC of *Amaranthus hybridus*for Cr in crude oil-polluted soil were < 1 while the BCF was >1.

Figures 1-5 show the phytoextraction potentials of the plant for remediation of Cu, Cr, Cd, Pb and Ni in crude oil-polluted and Control soils. Figure. 1 reveals that *Zea mays* had the highest phytoextraction potential (54.25) for Cu while *Abelmoschus esculentus* had the lowest (2.25) in crude oil-polluted soil, whereas in Control soil, *Zea mays* had the highest Cu phytoextraction potential (67.34), while *Tithonia diversifolia* had the least (31.70). Figure 2 shows the phytoextraction potential of the selected plants for Cr in the polluted soils. The phytoextraction potential was highest in *Zea mays* (441.87) and lowest in *Tithonia diversfolia* (175.12). On the other hand, in Control soil, *Abelmoschus esculentus* had the highest phytoextraction potential (174.46), while *Zea mays* had the lowest (72.15) of all the selected plants used. The phytoextraction potentials of the selected plants for Cd in the polluted soil are shown in Figure 3. *Zea mays* recorded the highest photoextraction potential (31.27) for Cd in Control soil, while *Amaranthus hybridus*had the least (9.77). In the crude polluted soil, *Amaranthus hybridus* had the highest phytoextraction potential (29.44), while *Tithonia diversifolia* had the least (0.99). Figure 4 shows the phytoextraction potentials of the selected plants for Pb in the crude oil-polluted soils. In the crude oil-polluted soil, *Zea mays* had the highest (461.12) phytoextraction potential, and *Amaranthushybridus* had the lowest potential for Pb. In Control, *Amaranthus hybridus* had the highest phytoexraction potential (212.66), whereas, *Tithonia diversifolia* recorded the least. Figure 5 shows the phtyoextraction potentials of the selected plants for Ni in crude oil-polluted and Control soils. The highest phytoextraction potential (301.25) for Ni in control soil was recorded in *Zea mays,* whereas, the lowest (74.42) was recorded in *Amaranthus esculentus.* On the other hand, the highest phytoextraction potential for Ni (487.37) in crude oil-polluted was obtained in *Zea mays,* while the lowest (166.98) was obtained in *Amaranthus hybridus.*

Table 5: Heavy metal dynamics in *Amaranthus hybridus* planted in crude oil-polluted and Control soils.

	Cu		Cr		Cd		Pb		Ni	
	CP	**Ctr**	**CP**	**Ctr**	**CP**	**Ctr**	**CP**	**Ctr**	**CP**	**Ctr**
BCF	3.00	1.87	1.31	0.63	0.38	1.38	0.55	2.94	0.81	1.04
TF	1.50	1.50	0.67	0.67	1.31	1.31	1.75	1.75	0.87	0.87
BAC	4.50	2.00	0.88	0.64	0.50	1.13	0.96	2.42	0.71	1.70

BCF: Biological Concentration Factor, TF: Translocation Factor, BAC: Biological Accumulation Coefficient, CP: Crude Oil-Polluted, Ctr: Control.

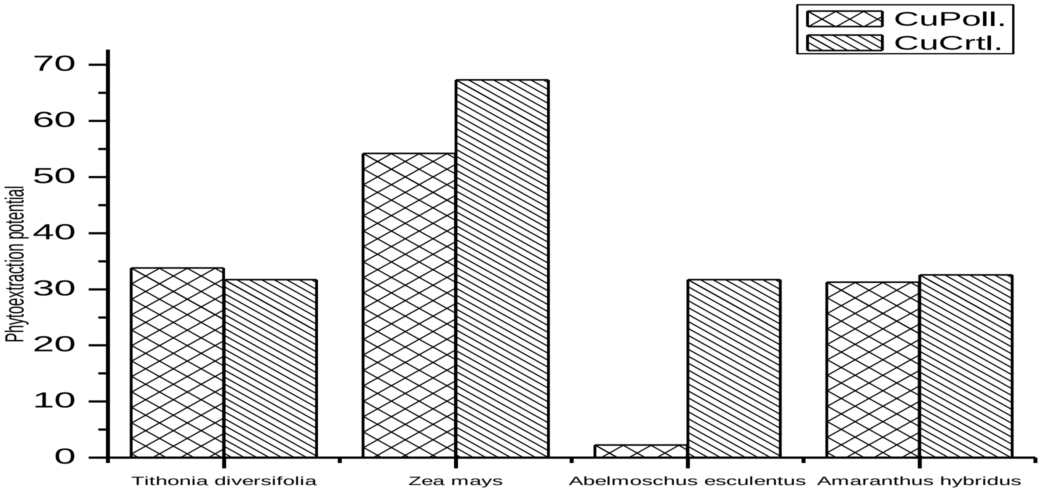

Fig. 1: Phytoextraction potential of the plants for Cu in the soils used for the experiment

Cu Poll= Phytoextraction potential for Cu in crude oil-polluted soil
Cu Ctrl= Phytoextraction potential for Cu in Control soil

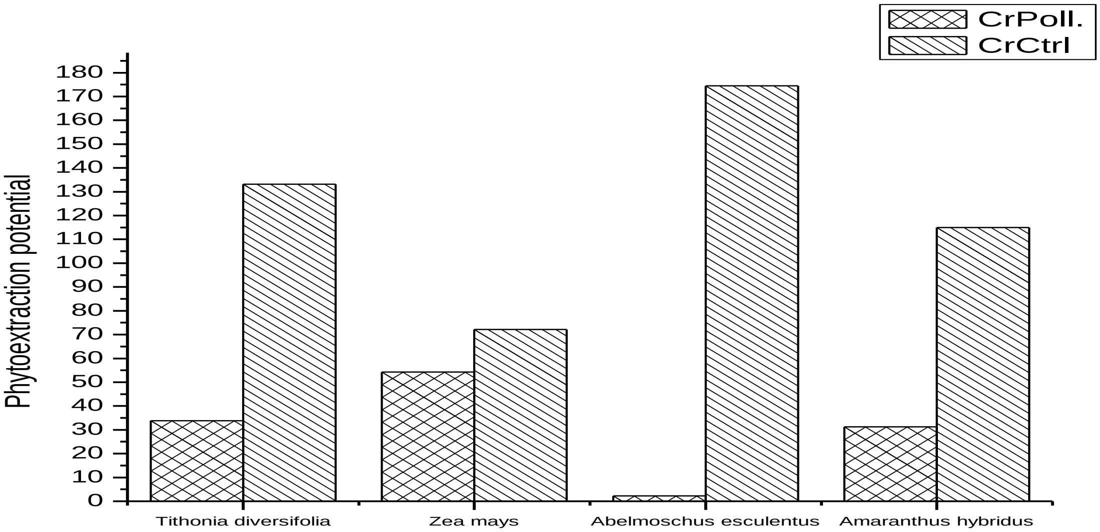

Fig. 2: Phytoextraction potential of the plants for Cr in the soils used for the experiment

Cr Poll= Phytoextraction potential for Cr in crude oil-polluted soil
Cr Ctrl= Phytoextraction potential for Cr in Control soil

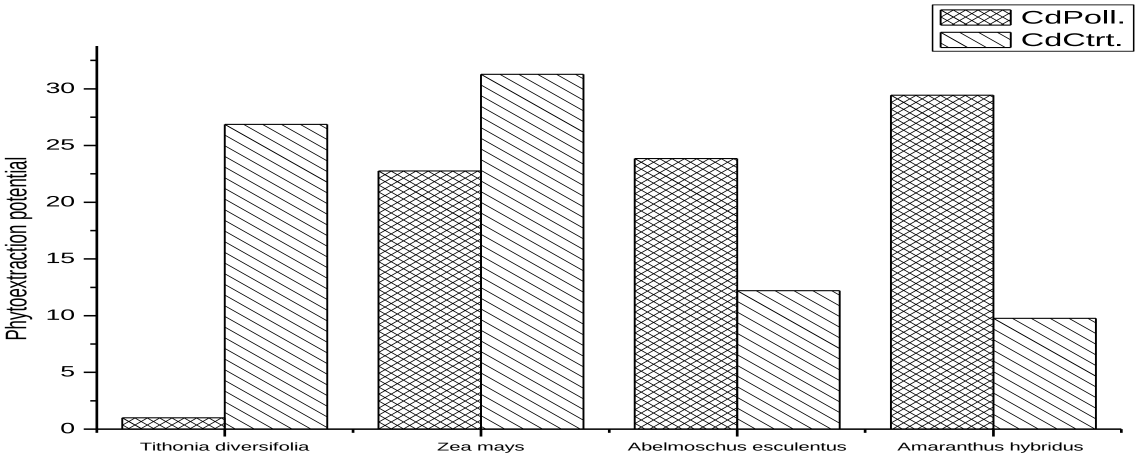

Fig. 3: Phytoextraction potential of the plants for Cd in the soils used for the experiment

Cd Poll= Phytoextraction potential for Cd in crude oil-polluted soil
Cd Ctrl= Phytoextraction potential for Cd in Control soil

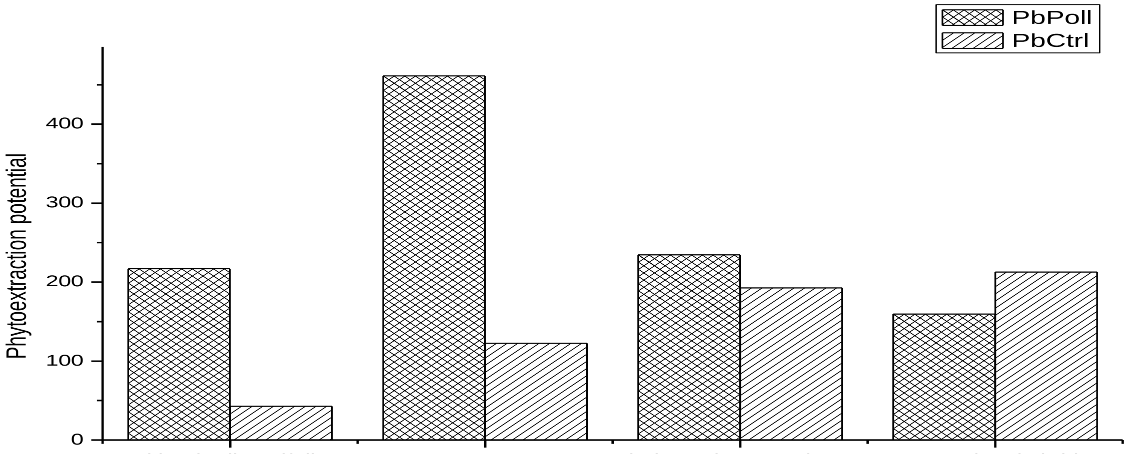

Fig. 4: Phytoextraction potential of the plants for Pb in the soils used for the experiment

Pb Poll= Phytoextraction potential for Pb in crude oil-polluted soil
Pb Ctrl= Phytoextraction potential for Pb in Control soil

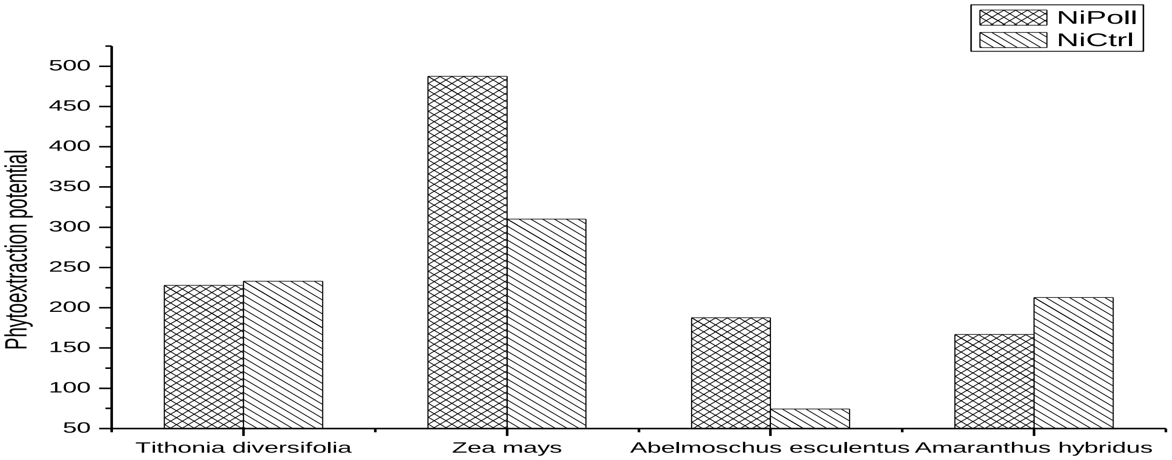

Fig. 5: Phytoextraction potential of the plants for Ni in the soils used for the experiment

Ni Poll= Phytoextraction potential for Ni in crude oil-polluted soil
Ni Ctrl= Phytoextraction potential for Ni in Control soil

Table 6 shows the phytoextraction efficiency of the selected plants in the polluted soil. The remediation factor of Cu varied from 0.008% in *Abelmoschus esculentus* planted in crude oil-polluted soil to 0.161% in *Tithonia diversifolia* planted in crude oil-polluted soil. The remediation factor for Cr ranged from 0.012% in *Amaranthus hybridus* planted in crude oil-polluted soil to 0.475% in *Abelmoschus esculentus* planted in crude oil-polluted soil and in *Abelmoschus esculentus* planted in Control soil. The phytoextraction efficiency of the selected plants for Cd in the polluted soils varied from 0.008% in *Zea mays* planted in crude oil-pollution soil to 0.611% in *Tithonia diversifolia* planted in Control soil. *Abelmoschus esculentus* had the highest remediation factor (0.007%) for Cd compared to other plants in crude oil-polluted soil, whereas, *T. diversifolia* had the highest remediation factor of the plants in Control soil.

The highest remediation factor for Pb (0.080%) was found in *Tithonia diversifolia* planted in crude oil-polluted soil, while the least remediation factor (0.013%) was found in *Tithonia diversifolia* planted in crude oil-polluted soil. In the Control soil, remediation factor for Pb was highest (0.075%) in *Amaranthus hybridus* and lowest (0.044%) in *Zea mays*.

The results showed that *T. diversifolia* was more efficient in remediating Pb in crude oil-polluted soil while *Amaranthus hybridus* was more efficient in Control soil when compared to other plants. The highest remediation factor for Ni (0.304%) was obtained in *Zea mays* for crude oil-polluted soil and lowest (0.009%) in *Amaranthus hybridus* in crude oil-polluted soil. In the Control soil, *Zea mays* had the highest remediation factor (0.662%) while *Abelmoschus esculentus* had the least (0.016%) remediation factor. This result revealed that *Zea mays* was the most efficient in remediating Ni in both crude oil-polluted and Control soils.

Table 7 shows the mean biomass of the plants grown in crude oil-polluted and Control soils. Each of the selected plants raised on soil without the crude oil had higher and greater biomass than the same plant raised in crude oil polluted soil. Student t-test revealed that there was statistical difference between the mean biomass of the selected plants raised in crude oil-polluted soil and control soil. The p-value was 0.003, therefore there was a significant difference in the biomass of *Tithonia diversifolia* raised in crude oil-polluted soil and Control soil at $p \leq 0.05$. The four plants showed significant differences in their biomasses based on the soil used. The biomasses of the plants raised in Control soil were statistically greater than those raised in crude oil-polluted soil.

Table 6: Phytoextraction efficiency (Remediation factor) of the selected plants in crude oil-polluted and Control soils.

	Remediation factor (%)									
Plant	**Cu**		**Cr**		**Cd**		**Pb**		**Ni**	
	CP	**Ctr**	**CP**	**Ctr**	**CP**	**Ctr**	**CP**	**Ctr**	**CP**	**Ctr**
Tithonia diversifolia	0.161	0.048	0.045	0.028	0.001	0.611	0.080	0.070	0.022	0.022
Zea mays	0.013	0.84	0.018	0.015	0.001	0.050	0.040	0.044	0.030	0.066
Abelmoschus esculentus	0.008	0.057	0.019	0.048	0.007	0.174	0.018	0.069	0.010	0.016
Amaranthus hybridus	0.059	0.062	0.012	0.020	0.007	0.035	0.013	0.075	0.009	0.053

CP: Crude Oil-Polluted, Ctr: Control.

Table 7: Comparison of the biomass of shoots and roots of plants in the polluted soils

Plants	**CP**	**Ctr**	**t-value**	**p-value**
Tithoniadiversifolia	2.47±0.97	4.36±1.33	4.543	0.003
Zea mays	2.37±0.87	6.26±2.04	3.206	0.015
Abelmoschus esculentus	1.05±0.45	2.77±0.85	4.062	0.005
Amaranthus hybridus	1.47±0.61	2.82±0.97	3.472	0.010

CP: Crude Oil-Polluted, Ctr: Control.

Discussions

Accumulation of heavy metals varied among plants species and the uptake of a metal by a plant is dependent on the plant species, its in-built controls, and the soil quality (Chunilall*et. al.*, 2005). A number of factors control heavy metal accumulation and bioavailability such as soil and climatic conditions, plant species and agronomic technic, active or passive transfer processes, sequestration, the type of plant root system and the response due to seasonal cycles. Structure of the sediment has also been considered very important as it affects the extent of the metals taken up by the plants (Kabata-Pendias and Pendias 1984). Clay particles also play an important role in availability of the metals. Metal solubility in soils is predominantly controlled by pH, and oxidation state of the system (Ghosh and Singh 2005).

The Translocation Factor (TF) was calculated as the ratio of shoot to root. It indicated internal metal transportation. Translocation factors greater than one showed that metals were effectively translocated to the shoot from the root. It can be seen that at different treatments the TF values for the metals are greater than one while at other treatments we have TF<1. TF>1 showed that metals were effectively translocated to the shoot from root. This observation is similar to the observations by Sun *et al*. (2008) on *Solanum nigrum* plant.

The Biological Accumulation Coefficient (BAC) value was calculated as the concentration of metal in the plant shoot divided by the concentration of the metal in the soil. The BAC represents the concentration of the metal in plants compared with the concentration in the soil. For efficient phytoremediation, the BAC has to be greater than 1. BAC>1 are indicative of metal accumulating in the above-ground part of the plant.

Biological Concentration Factor (BCF) was calculated as metal concentration ratio of plant roots to soil. Plants that are Accumulators had TF > 1 or BAC > 1, Indicators had metals in their tissue similar to those in the surrounding soil, Excluders had TF < 1 while Phytostabilizers had BCF > 1 but TF < 1.

*Tithoniadiversifolia*is suitable for the extraction of Cu and Pb in both soils, phytoextraction of Cr in crude oil-polluted soil and phytoextraction of Cd in Control soil but less suitable for the phytoextractrion of Cr in Control soil, less suitable for phytoextraction of Cd in crude oil-polluted soil and less suitable for phytoextraction of Ni in both soils. *T. diversifolia* is an accumulator of Cr and Pb but stabilizer of Cu in crude oil-polluted soil. It is also a phytostabilizer of Cu, Cd, Pb in Control soil (soil without crude oil). The Control soil may have been probably polluted by flood from the river or run-off from the power station nearby.

Zea mays is an accumulator of Cu, stabilizer for Pb and Ni in crude oil-polluted soils. Cd and Ni are both excluded by *Zea mays* in Control soil an excluder of Cr and Cd in crude oil-polluted soil. *Zea mays* showed suitability for Cr accumulation in Control soil with TF > 1 but less suitable for Pb extraction in Control soil with BCF, TF and BAF < 1. *Abelmoschus esculentus* is suitable for phytoextraction of Cu, Cr and Pb in both Control and crude oil-polluted soils, while it could only phytostablize Ni and Cd in Control soil. In addition, *A. esculentus* proved suitable for Cd phytoextraction in crude oil-polluted soil but less suitable for Ni extraction in crude oil-polluted soil.

A. hybridus is an accumulator of Cu for both crude oil-polluted and Control soils, Cd and Pb for Control soil, stabilizer of Cr and Ni of crude oil-polluted and Control soils respectively and an excluder for Cr and Ni for Control soil. Johnson *et al.* (2009) investigated the potentials of *Tithoniadiversifolia*and *Helianthus annus* (species of Sunflower) to remove heavy metals from polluted soil. Their results showed that *T. diversifolia* and *Helianthus annus* extracted substantial concentration of Pb in the above-ground biomass compared to the concentration in the roots and that the efficiency of *Tithonia diversifolia* and *Helianthus annus* in cleaning the polluted soil was at the early stage of their growth.

Dahiru*et al.* (2014) investigated the potential of *Telfairia occidentalis* for phytoremediation of soil polluted with Cd, Cu, Pb, Cr and Co. The plant's shoot contained more Cd, Cu, Pb, Cr and Co than the roots. They stated that these metals were mostly translocated to the shoot following absorption by the roots.

Cadmium (Cd) is a toxic element and exists along with Zn in nature. The results indicated that Cd could be accumulated in all the parts of the plants (shoots and roots). The distribution of Cd within plant organs is quite variable and clearly shows its rapid translocation from roots to shoots (Kabata-Pendias, 2001). The present study classifies *Tithonia diversifolia*, *Abelmoschus esculentus*, *Amaranthus hybridus* and *Zea mays* as cadmium accumulators. These species were able to phytoextract Cd above the permissible level. This could be because of the organic matter content of the soil and acidic nature of the soil. The permissible limit of Cadmium in plants, recommended by WHO is 0.02 mg kg-^{1}.The maximum permissible limit of Cd in the soil according to SEPA of China is 0.6 mg kg-^{1}. The concentration of cadmium in the soil sample used was above maximum permissible limit (MPL) (0.6 mg kg-^{1}) (SEPA 1995).

Voogt*et al.* (1980) upheld that Cd can be taken up by plant such as maize, spinach, wheat and rice. It is capable of accumulating in food chains and its uptake is irrevocable and its excretion is very slow, it is therefore very toxic in nature. Uba*et al.* (2008) in their assessment of heavy metals bioavailability discovered that extractable Cadmium was found to be above the critical permissible concentration of 3.0 mg kg-^{1}. The findings in this study corroborated the work of Egberongbe (2010) who reported that *Tithonia diversifolia* seedlings absorbed Cd and Pb in polluted soils, and the contents in the root were more than the contents in the shoot.

Wagh *et al.* (2013) pointed out that Cu content of most plant is generally between 2 and 20 mg/kg in the plants as Cu strongly binds to soils it is very immobile and hence the plant roots are frequently higher in Cu concentration than other plant tissues. This could be why more Cu concentrations were found in the roots of the plants used for this study.

The results in this study is consistent with the findings of Motesharezadeh and Savaghebi-Firoozabadi (2011) who observed the highest concentration of nickel in shoot of *Amaranthus* (176.83 mg/kg) and in the root of alfalfa (462.73 mg kg-^{1}).

The findings in this work also corroborates of the work of Bigaliev*et al.* (2000) who worked on the capabilities of *Amaranthus* in phytoremediating soils polluted with Zn, Cd, Cu and Ni. Bigaliev *et al.* (2000) observed that the two species of Amaranthus had delay in seed germination, reduced wet weight of the shoots and roots. *Amaranthus* is this study has one of the least roots and shoots fresh and dry weights. This could be because of the effect of the crude oil toxicity.

Madejon*et al.* (2003) examined the potential of sunflower in phytoremediation soil polluted with As, Cd, Cu and Ti, and concluded that the amount of these metals absorbed by the plant is meaningfully more in polluted soil than in the unpolluted one; and metals such as As was higher in roots than shoots, while Cd was observed more in the shoots than in the roots.

Abou-Shanab*et al.* (2006) studied the potential of some plants for remediating heavy metals-polluted soils. In their investigation, sunflower, maize, sorghum, Bermuda grass and alpine fleabane were selected because of high production of biomass, fast growth and capability of removal of metals from polluted places. They also found that the biomass produced by these plants decreased by increasing the concentration of the heavy metals. These findings are similar to the findings in this work.

Conclusion

This study has revealed the potentials of *Amaranthus hybridus*, *Tithonia diversifolia*, *Abelmoschus esculentus*and *Zea mays* for remediatingCu,Cr, Cd Pb and Ni polluted soils and are therefore recommended for their biorestitution.

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