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Phytoremediation Potentials of *Terminalia Mantaly* H. Perrier for Heavy Metals and Hydrocarbon Removal from Spent Engine Oil Contaminated Soil

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Abstract

The study analyzed the phytoremediation of heavy metals and Total Hydrocarbon in spent engine oil contaminated soils using seedlings of *Terminalia mantaly*. 2.5kg of soil samples were contaminated with 25ml, 50ml, and 75ml levels of spent engine oil respectively. The experimental design was Completely Randomized Design and data was analyzed using descriptive statistics and ANOVA at $p < 0.05$. The analyzed soil samples revealed the presence of Cu, Zn and Cd. 25ml plant samples bioremediated more of Cu (539.13%), 50ml plant sample (65.15%; 94.39%) bioremediated more of Zn, THC and Cd respectively. The shoot of 50ml plant samples ($9.22^a \pm 0.04$; $42.81^a \pm 0.11$) bioaccumulated higher amount of Cu and Zn, while 25ml SEP ($10.03^a \pm 0.04$) bioaccumulated more of Cd in their shoot. 75ml plant samples ($0.54^a \pm 0.01$) bioaccumulated more of Cu and THC in their roots respectively. For heavy metals and THC bioaccumulation in the leaves, 50ml plant samples ($8.91^a \pm 0.06$; $68.94^a \pm 0.19$) was highest for Cu and Zn, while the highest for Cd was in 25ml plant samples ($5.87^a \pm 0.04$) which was not significantly different from 50ml plant samples ($5.83^a \pm 0.05$). The results showed that *Terminalia mantaly* has great potentials for remediating contaminated soils. The uptake of heavy metals with its vegetative parts suggests its ability to survive in toxic conditions. Therefore, the species is recommended for phytoremediation of spent engine oil contaminated sites.

Keywords: Phytoremediation, Bioaccumulation, Spent Engine Oil, Total Hydrocarbon Content, Heavy Metals, Environmental Restoration.

Introduction

One of the biggest global issues brought on by the use of fossil fuels in numerous industries to power machinery is pollution. Conforming to Chen and Chen (2001), a number of businesses are to blame for the natural release of heavy metal pollutants as Lead, Zinc, Cadmium, Nickel and Copper. Additionally, the usage of fossil fuels has been linked to significant environmental contamination, particularly in light of the growing global population. As indicated by Wyszowski and Zilkowska (2008) and Agbogidi and Enujeke (2012), oil contamination, characterized as the alteration of a natural ecosystem by liquid molecules of hydrocarbons is hazardous to plants and animals and decreases the productivity of terrestrial and aquatic ecosystems. Engine oils are one prominent petroleum derivatives of crude oil that are contributors to ecological pollution. Residual vehicular oil, also known as spent engine oil, is frequently gathered from lubrication-change stores, parking lots, and industries that feature compressor oil, processor oil, and metal-working liquids. Due to its liquid nature, spent engine oil has the propensity to migrate into the environment, ultimately leading to its contamination of either water or soil. Copper, lead alloys, arsenic, zinc, cadmium, and a variety of toxic metals are captured up by oil in engines as it rotates, along with other contaminants. Being that it receives contamination by so many dangerous substances and metallic elements during usage, residual oil is categorized as a carcinogenic liquid. Whether unintentional or deliberate, the discharge of spent oil into the ecosystem endangers a combination of

aquifers and exterior bodies via the presence of oil. This exposes the public's water source in peril and jeopardizes marine life. Oil may impair aquifers whenever it is eliminated off inappropriately, for as by pouring it down sewers or into the soil itself. Interestingly, single units of wasted oil will the capacity to foul up to a million units of water. When motor oil leaks from a machine, it can be extensively disseminated into the ambient air before eventually entering wetlands by overflow. Residual engine oil is venomous to both fauna and plants when it is present in rivers, and because it forms an opaque substance on the outermost layer of water, it can obstruct vital biological reactions like photosynthesis and oxygen refreshment. Additionally, potable water and soils can be contaminated by spent engine oil that in turn reduces the productiveness of the soil. These contaminants not only diminish the availability of the soil's oxygen but also alter its physiochemical properties. Furthermore, having a detrimental impact on micro and macroorganisms present in the soil, leading to their destruction.

Several authors have worked on the phytoremediation of diesel polluted soil using seedlings of *Khaya senegalensis* and *Terminalia superba*, (Olajuyigbe *et al.*, 2019). Olayiwola *et al.*, (2021) examined the bio-accumulation of heavy metals of *Terminalia superba*, *Tectona grandis*, *Terminalia ivorensis*, *Gmelina arborea* and *Shorea roxburghii*. Emmanuel *et al.*, (2019) determined the phytoremediation of heavy metals in soils polluted with spent engine oil using *Senna alata*, while Adio *et al.*, (2016) examined the phytoremediation capabilities

of *Mansonia altissima*, *Entandrophragma angolense* and *Terminalia superba* but none has worked on the use of *Terminalia mantaly* for the phytoremediation of spent engine oil polluted soil.

This research aims to identify the quantity of heavy metals (copper, zinc and cadmium) and total hydrocarbons present in various levels of spent engine oil-contaminated soils before and after the study and to determine the number of heavy metals and total hydrocarbons accumulated by the leaves, shoots, and roots of *Terminalia mantaly* seedlings in the contaminated soil.

MATERIALS AND METHODS

The investigation was performed in the Department of Forestry and Environment nursery, Rivers State University, Port Harcourt, Rivers State. The institution is situated in southern region of Nigeria, Located at latitude 4° 42' and 4° 48' N; Longitude 6° 15' and 7.25° E. It is 18m above sea level with a yearly temperature which varies from 21.3°C – 31.2°C and annual rainfall of 2000 – 2476mm with a bio-modal distribution (Nwisiutor, 2013). Seven (7) months old seedlings of *Terminalia mantaly* were acquired from the Department of Forestry and Environment nursery, Rivers State University. The spent engine oil (Total brand Engine oil) was obtained from a mechanical workshop, located at G.U Eke Road, Eligbolo community of Rivers State.

Soil sample of about 2.5kg was collected from the nursery and sieved to eliminate particles. It was carefully mashed and infused with spent engine oil at different contamination levels consisting of 25ml, 50ml, 75ml and a control soil (which was not contaminated). Three seedlings per treatment were for the experiment. The seedlings were subsequently transplanted into polythene pots with the various soil treatments for the experiment and they underwent sixteen weeks of monitoring. The experimental design that was used in this study was completely randomized design (CRD).

The treatments breakdown is as follows;

T₁: 25ml Spent engine contaminated soil

T₂: 50ml Spent engine contaminated soil

T₃: 75ml Spent engine contaminated soil

T₀: Control soil

Data obtained were analyzed using descriptive statistics summarized on tables, graphs, and inferential statistics, using one-way analysis of variance (ANOVA) at 5% level of significance. Duncan New Multiple range test was to separate the means of the variables that were significant.

Heavy metals analysis (copper, zinc and cadmium) was carried out on all the soil treatments at the commencement of the experiment and this was done on day fourteen (14) after pollution to allow for effective mineralization and also the same heavy metals analysis was carried out at termination of the experiment. The concentration of heavy metals in the soil samples was analyzed with Atomic Absorption Spectrometer (AAS) (Nwaichi, *et al.*, 2021).

The seedlings from each treatment were destructively sampled at the end of the experiment; the plants were uprooted, cleaned out and segmented into three sections (roots, stems, and leaves). The samples were milled into a smooth particle using a wooden mortar and oven-dried at 60°C (Frasier *et al.*, 2016). Each milling component was completely blended, homogenized, and placed in polythene bags until acid digestion.

The samples were then kept on a 250ppm digestion tube and 10ml of Nitric acid (HNO₃) was added. It undergoes heating for 45mins at 90°C, the temperature was increased to 150°C and followed by boiling for eight hours until a transparent solution was achieved. Heavy metal analysis was carried out using Buck Atomic Absorption Spectrophotometer to discover the concentration of heavy metals in the samples. The range of the concentration and detection limits for Cu, Zn and Cd is 0.005 – 0010mg/L, 0.005mg/L and 0.01mg/L respectively. The Buck Certified AA Standard calibration was adopted (Buck Scientific Manual, 2005).

Total Hydrocarbon was determined using a method adopted by Odu *et al.*, (2006). Soil samples of 10g were combined with 10ml of toluene. The hydrocarbon was processed and identified by the absorbance of the extract at 420nm using spectrophotometer standard curve of the absorbance of the different known concentration of the spent engine oil in the samples which was drawn first after reading from the spectrophotometer.

The heavy metals remediated were calculated using the formula;

Amount Remediated (AR_(Parameter)) = Initial Concentration (Ic) – Final Concentration (Fc)

$$\% \text{ Bioremediation} = \frac{AR}{Ic} \times 100$$

$$\text{Bioaccumulation Factor (B.F)} = \frac{Cp}{Cs}$$

Where: Cp refers to Metal Concentration in whole Plant tissues and Cs refers Initial Concentration of metal in the soil.

RESULTS

Results from the analysis carried out on the various soil treatments before the experiment showed that there were significant differences in the levels of Copper (Cu), Zinc (Zn), Cadmium (Cd) and Total Hydrocarbon (THC) present in the soils. Treatment 75ml (T3) recorded a higher level of Zn (50.00^a ±0.001) and THC (1402.00^a ±0.006), while Treatment 50ml (T2) was highest for Cu (1.32^a ±0.02) and Cd (9.92^a ±0.02). The result is presented in table 1.

Table 1: Heavy Metals (µg/g) and THC (mg/kg) in soil before the experiment

VARIABLES	Cu	Zn	Cd	THC
T1 (25ml)	0.23 ^c ±0.25	25.07 ^c ±0.12	5.82 ^c ±0.15	935.34 ^c ±0.02
T2 (50ml)	1.32 ^a ±0.02	46.00 ^b ±0.001	9.92 ^a ±0.02	1202.00 ^b ±0.006
T3 (75ml)	0.81 ^b ±0.02	50.00 ^a ±0.001	9.72 ^b ±0.15	1402.00 ^a ±0.006
T0 (Control)	0.01 ^d ±0.01	2.72 ^d ±0.02	0.81 ^d ±0.15	2.00 ^d ±0.00

Means with same superscript across column are not significantly different at p=0.05

*=significant (p< 0.05)

At termination of the study, the soil samples were analyzed again to show the level of heavy metals and THC left in the soil. The result showed a significant difference ($p<0.05$) in the levels of Copper (Cu), Zinc (Zn), Cadmium (Cd) and Total Hydrocarbon (THC). Treatment 25ml (T1) had a lesser level of heavy metals for Cu ($-1.01^b \pm 0.01$), Zn ($9.72^b \pm 0.07$) and Cd ($3.14^b \pm 0.02$). While Treatment 50ml (T2) was lesser for THC ($67.32^b \pm 0.01$). The result is presented in Table 2.

Table 2: Heavy Metals ($\mu\text{g/g}$) and THC (mg/kg) in soil after the experiment

VARIABLES	Cu	Zn	Cd	THC
T1 (25ml)	$-1.01^b \pm 0.01$	$9.72^b \pm 0.07$	$3.14^b \pm 0.02$	$178.44^d \pm 0.02$
T2 (50ml)	$-2.24^c \pm 0.01$	$16.03^c \pm 0.03$	$4.65^c \pm 0.01$	$67.32^b \pm 0.01$
T3 (75ml)	$-0.58^b \pm 0.02$	$44.13^d \pm 0.02$	$6.22^d \pm 0.04$	$111.76^c \pm 0.02$
T0 (Control)	$-0.07^a \pm 0.05$	$0.04^a \pm 0.01$	$0.12^a \pm 0.02$	$0.65^a \pm 0.02$

Means with same superscript across column are not significantly different at $p=0.05$

*=significant ($p<0.05$)

The %Bioremediation for the heavy metals and THC in the soil was calculated after the initial concentration and final concentration was gotten. Table 3 shows the results.

Table 3: %Bioremediation of Heavy Metals and THC

SAMPLES	Cu	Zn	Cd	THC
T1 (25ml)	539.1304	61.22856	46.04811	80.92245
T2 (50ml)	269.697	65.15217	53.125	94.39933
T3 (75ml)	171.6049	28.93082	58.00204	92.03421
T0 (Control)	79.33492	11.74	36.00823	37.5

The result in Table 4 indicated a significant difference ($p<0.05$) in the levels of heavy metals (Cu, Zn, Cd) that was accumulated by the shoot of the plant under the different soil treatments. Treatment 50ml (T2) was highest for Cu ($9.22^a \pm 0.04$) and Zn ($42.81^a \pm 0.11$). While Treatment 25ml (T1) was highest for Cd ($10.03^a \pm 0.04$).

Table 4: Heavy Metals ($\mu\text{g/g}$) and THC (mg/kg) in the shoots of *Terminalia mantaly*

VARIABLES	Cu	Zn	Cd	THC
T1 (25ml)	$4.42^c \pm 0.02$	$22.06^b \pm 0.03$	$10.03^a \pm 0.04$	$0.47^a \pm 0.03$
T2 (50ml)	$9.22^a \pm 0.04$	$42.81^a \pm 0.11$	$4.27^c \pm 0.03$	$0.49^a \pm 0.01$
T3 (75ml)	$6.63^b \pm 0.44$	$21.24^c \pm 0.02$	$4.91^b \pm 0.03$	$0.46^a \pm 0.02$
T0 (Control)	$1.22^d \pm 0.04$	$1.77^d \pm 0.16$	$1.02^d \pm 0.02$	$0.07^b \pm 0.03$

Means with same superscript across column are not significantly different at $p=0.05$

*=significant ($p<0.05$)

The result revealed a significant difference ($p<0.05$) in the levels of heavy metals (Cu, Zn, Cd) and THC that was accumulated by the plant's root under the different soil treatments. Treatment 25ml (T1) was highest for Zn ($32.11^a \pm 0.04$) and Cd ($7.04^a \pm 0.02$). While Treatment 75ml (T3) recorded a higher level of Cu ($503.08^a \pm 0.03$) and THC ($0.54^a \pm 0.01$). This result is presented in Table 5

Table 5: Heavy Metals ($\mu\text{g/g}$) and THC (mg/kg) in the roots of *Terminalia mantaly*

VARIABLES	Cu	Zn	Cd	THC
25ml	$2.45^b \pm 0.02$	$32.11^a \pm 0.04$	$7.04^a \pm 0.02$	$0.42^b \pm 0.01$
50ml	$2.23^c \pm 0.03$	$30.72^b \pm 0.03$	$4.26^c \pm 0.02$	$0.42^b \pm 0.02$
75ml	$3.08^a \pm 0.03$	$28.94^c \pm 0.27$	$6.84^b \pm 0.02$	$0.54^a \pm 0.01$
Control	$1.02^d \pm 0.08$	$2.68^d \pm 0.24$	$1.46^d \pm 0.04$	$0.08^c \pm 0.02$

Means with same superscript across column are not significantly different at $p=0.05$

*=significant ($p<0.05$)

The result indicated a significant difference ($p<0.05$) in the levels of heavy metals (Cu, Zn, Cd) and THC that was accumulated by the leaves of the plant under the different soil treatments. This result is represented in Table 6.

Table 6: Heavy Metals ($\mu\text{g/g}$) and THC (mg/kg) in the Leaves of *Terminalia mantaly*

VARIABLES	Cu	Zn	Cd	THC
25ml	$4.02^b \pm 0.01$	$41.86^b \pm 0.04$	$5.87^a \pm 0.04$	$0.95^b \pm 0.02$
50ml	$8.91^a \pm 0.06$	$68.94^a \pm 0.19$	$5.83^a \pm 0.05$	$0.87^c \pm 0.01$
75ml	$1.22^c \pm 0.02$	$15.67^c \pm 0.03$	$3.38^b \pm 0.03$	$1.16^a \pm 0.01$
Control	$0.34^d \pm 0.03$	$1.23^d \pm 0.09$	$1.04^c \pm 0.07$	$0.07^d \pm 0.01$

Means with same superscript across column are not significantly different at $p=0.05$

*=significant ($p<0.05$)

Bioaccumulation Factor (B.F)

The Bioaccumulation Factor of *Terminalia mantaly* was estimated as a ratio of the concentration of Heavy metals in the whole plant (Shoot, root and leaves) and the initial soil concentration. A bioaccumulation factor More than 1 implies that the plant is suitable for phytoremediation. The result is presented in Table 7.

Table 7: Bioaccumulation Factor of Heavy Metals and THC

SAMPLES	Cu	Zn	Cd	THC
25ml	37.78261	3.830475	3.941581	0.001967
50ml	15.42424	3.118913	1.447581	0.001481
75ml	13.49383	1.317	1.556584	0.00154
Control	1.890736	6.578616	1.041794	0.00010

DISCUSSION

The issue of oil contamination is getting worse and it has impacted various nations that produce oil, particularly Nigeria. The pollution of vegetation and the overall ecological system by spent engine oil have had detrimental effects, as highlighted in a study by Odukayo *et al.*, (2019). Despite the fact that it contains aliphatic and aromatic chemicals, additionally, it possesses contaminants like cadmium, lead, copper, zinc, and certain trace elements like nickel, iron, and aluminum (Wilberforce, 2016).

The THC and heavy metals (Cu, Zn and Cd) in the soil samples decreased notably after phytoremediation. It was observed that the control soil (gotten from the nursery) also had some little levels of heavy metals present in them and very minute trace of THC. This reveals that heavy metals occur naturally in the soil in the forestry nursery but becomes more toxic when present in high proportions.

The decreased of heavy metals and THC noticed in the soil after the experiment suggests that *Terminalia mantaly* was efficient at absorbing heavy metals and THC into its system. The uptake of Cu, Zn and Cd is also an indication that *Terminalia mantaly* has the potentials of remediating areas with low to medium contamination of spent engine oil. This was evident by the continued and surviving ability, although with a diminished plant growth in the contaminated soils. The optimal bioremediation achieved by the plant when compared to the treatment with higher concentration could be potentially due to phytotoxicity at higher contamination levels.

Terminalia mantaly was an effective hyperaccumulator of Cu, Zn, Cd and THC, this is in agreement with the investigation of Messou *et al.*, (2012).

The capacity of *Terminalia mantaly* to flourish in soils containing spent engine oil infers that the species may be able to disintegrate or dissipate the toxins. This is due to the fact that biomass buildup continued regardless of the contaminants' restriction on vegetative growth (Lone *et al.*, 2008). This study has successfully shown that alongside other indigenous species that has been discovered and recommended by some authors for phytoremediation of oil polluted areas (Olajuyigbe and Aruwajoye, 2014; Olajuyigbe and Sijuola, 2015), as well as in Nwaichi *et al.*, (2021). *Terminalia mantaly* was able to bioaccumulate Cu in the polluted soil in an increasing order of Root<Leaves<Shoot. Zn was in an increasing order of Shoot<Root<Leaves, Cd recorded an increasing order of Leaves<Root<Shoot and THC was bioaccumulated in an increasing order of Root<Shoot<Leaves. Control bioaccumulated the heavy metals present in an increasing order of Root<Leaves<Shoot; Leaves<Root<Shoot and Shoot<Leaves<Root for Cu, Zn and Cd respectively.

CONCLUSION

Terminalia mantaly showed great potentials based on its modest phytoremediation potentials as the seedlings were able to attain comparable values in the study period with the control based on the results from the experiment. The tropical tree species proved tolerant of spent engine oil concentration levels as high as 75ml, thus with more studies, it would be possible

to explore this species as an ideal option for ecological restoration of polluted areas. To prevent harm to biological diversity, this plant should be destroyed following phytoremediation. Additionally, there is a requirement to develop ways to recycle spent engine oil rather than discard it carelessly because the undetermined consequences of this pollution could pose a major harm to both current and subsequent generations. A major limitation of this study is the short experimental duration; it is recommended that similar research be done on the species to span through the sapling/matured stage in order to ascertain the trend displayed herein. This work has been able to identify *Terminalia mantaly* as a suitable tree species for phytoremediation of spent engine oil polluted lands; hence it will be an addition to other species that has already been identified by other authors for phytoremediation and bioremediation processes.

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