Assessment of Heavy Metals on Selected Crops on Polluted Soil Amended with Organic and Inorganic Materials and Associated Health Risk

Chuku, O.S.[1], Ekweozor, I.K.E.[2], Anaero- Nweke, G.N.[3]

Department of Animal and Environmental Biology, Rivers State University, Port Harcourt, Nigeria

Abstract: ***An experiment was conducted in Rivers State University Research farm, Port Harcourt, to investigate the potentials of Leaf-litter and Hydrogen peroxide as bioremediators for Crude oil polluted soils. The experiment was arranged in a Block Design with various levels of pollution. The experiment had 14 treatments and 5 replicates: T1:100ml C/O + 100ml H_2O_2, T2:100ml C/O + 100g l/l, T3:200ml C/O + 200ml H_2O_2, T4:200ml C/O + 200g l/l, T5:300ml C/O + 300ml H_2O_2, T6:300ml C/O + 300g l/l, T7:400ml C/O +400ml H_2O_2, T8:400ml C/O + 400g l/l, T9:500ml C/O + 500ml H_2O_2, T10:500ml C/O + 500g l/l, T11:no pollution + 500ml H_2O_2, T12:no pollution + 500g l/l, T13:500ml C/O + no amendment and T14:control. Garden-egg, Beans and cucumber seeds were used as test crops. Viability test was carried out. 420 experimental bags of 10kg capacity were filled with 10kg soil and polluted with C/O at different levels, 140 bags for each plant. Organic and Inorganic manure were applied at 1 month interval after pollution for 4 months, and planting was done afterwards. Soil samples were analyzed for heavy metals. Result of soil analysis showed high levels of heavy metals which includes copper, lead and zinc after pollution and was deficient of essential macronutrients like phosphorus, potassium, nitrate etc (Lead:T1-T10 and T13=70-97, and T11,T12 and T14=22.0-28.0; Copper:T1-T10 and T13=17.0-22.0, and T11,T12 and T14=11.0-12.0; Zinc: T1-T10 and T13=28.1-31.0, and T11,T12 and T14=3.4-9.0; In the polluted soil which reduced to acceptable limits on the soils with the three crops after harvest (Lead: Org:T2-T10=0.11-0.19, Lead Inorg:T1-T9=0.16-0.32, T13=0.12-0.53, T11,T12 and T14=0.02-0.2 Copper: Org T2-T10=7.4-11.6 and Inorg:T1-T9=8.7-11.4, T13=10.7-11.5,T11, T12 and T14=2.1-9.5: Zinc: Org T2-T10=1.8-2.2 and Inorg:T1-T9=1.9-2.2, T13=1.6-2.3, T11,T12 and T14=0.4-1.4. Application of Leaf Litter Manure and H_2O_2 greatly degraded the PAHs in the soil thereby causing a reduction in soil heavy metals. Beans performed better in Leaf Litter amended soils than H_2O_2 amended soils, while cucumber and garden egg had poor yield in both leaf litter and hydrogen peroxide amended soils. Therefore, the use of leaf litter manure for the remediation of petroleum contaminated soil should be encouraged as this proved to amend the soils.***

1. Introduction

Pollution is defined as the production and release through human activities, of any substance into the environment, in quantities which are harmful to man, other living things or in some way reduce the quality of human life. These substances which make the environment impure are called pollutants. Ndukwu *et al*., (2012).

Crude Oil Pollution as "the introduction of crude oil or its by-products with other gases associated with it into the environment in quantities that are poisonous or capable of causing immediate physical, chemical and biological damage to the affected ecosystem". Tanee and Anyanwu (2007). Henry and Heinke, (2005) discussed the enormity of toxicity resulting from spilled oil on crop performance on aquatic plants, which is been adversely affected lately.

Heavy metals are considered one of the major sources of soil pollution. Heavy metal pollution of the soil is caused by various metals, especially Cu, Cd, Zn, Pb. (Karaca, *et al.*, 2010).

Heavy metals exert toxic effects on soil microorganism hence results in the change of the diversity, population size and overall activity of the soil microbial communities (Asharaf and Ali 2007). Elevated Pb in soils may decrease soil productivity and a very low Pb con concentration may inhibit some vital plant processes i.e. photosynthesis, mitosis and water absorption with toxic symptoms of dark green leaves, wilting of older leaves, stunted foliage of brown short leaves (Bhattacharyya, *et al.*, 2008). The metal plant uptake from soils at high concentration may result in a great health risk considering food-chain implications (Jordao, *et al.*, 2006). Uptake of heavy metals by plants and subsequent accumulation along the food-chain is a potential threat to human health. The consumption of heavy metal contaminated food can seriously deplete some essential nutrients in the body that are further responsible for decreasing immunological defences, intrauterine growth retardation, disabilities associated with malnutrition and high prevalence of upper gastro-intestinal cancer rates. (Khan, *et al.*, 2008)

2. Materials and Method

Experimental site

Rivers State University Teaching and Research farm, Port Harcourt with latitude of 4.7923 and a longitude of 6.9825. The study site is characterized by tropical monsoon climate with mean annual temperature of 32.15^{0}C, 66% humidity and 0.9948 atmospheric pressure, while, the soil is usually sandy or sandy loam underlain by a layer of impervious pan. The study site was situated at the Rivers State University Research Farm which functions under the Faculty of Agriculture, Rivers State University, Port Harcourt, Nigeria. An area of 20m x 10m was marked out with a measuring tape and then cleared to ground level. No covering was made so as to ensure sunlight had a direct focus on it, and rain to get to the plant. It represented a natural environment for proper and adequate growth.

Planting Materials

Treated seeds of garden egg (*Solanum melongena*), beans (*Phasseolus vulgaris*) and cucumber (*Cucumis sativus*) were the planting materials used for the experiment. They were

Licensed Under Creative Commons Attribution CC BY

obtained from ADP (Agricultural Development Programme) Rumuokoro, Port Harcourt, and Rivers State, Nigeria.

Experimental bags

A total of 420 experimental bags filled with soil were used for the whole experiment. 70 experimental bags were used for each plant which was replicated 2 times for the three (3) plants. The experimental bags were purchased from mile 3 market, Port Harcourt, and were equivalent to 10kg weight which was punctured on all sides and beneath so as to prevent water logging of the experimental bags.

Crude oil

100 litres of crude oil was purchased from the Port Harcourt Refinery, Eleme, Rivers State, which was then conveyed to the Rivers State University Research Farm and applied as a pollutant on the agricultural soil.

Measuring cylinder

A measuring cylinder of 1000ml capacity of different concentrations was used to measure crude oil used for polluting the soil.

Fertilizer

Organic and inorganic fertilizers were used to carry out this experiment. The organic fertilizer used here was *Terminalia catappa* (leaf litter) while the inorganic fertilizer was Hydrogen peroxide (H_2O_2). The *Terminalia catappa* was obtained from a site in the Rivers State University while the hydrogen peroxide was obtained from a scientific supply shop in Alakahia, Port Harcourt. The leaf litters were gathered in very large quantities, dried in the University of Port Harcourt green house and analysed before use.

Soil Samples and Treatment

Samples of soil were collected by composite sampling using a metal soil auger. Samples of the soil were brought together, homogenized and 10kg measured into experimental bags with perforations (Onuh *et al.*, 2008a) for both the first, second and third block. The soil parameters (copper, lead and zinc) were also determined in the Department of Plant Science and Biotechnology Laboratory, University of Port Harcourt. The process was carried out seven (6) times; before pollution, after pollution, 1 months after amendment for a period of 4 months, and health risk assessment was carried out on the fruits after harvest.

For the treatment, 10kg of soil was weighed into labelled punctured experimental bags (Onuh *et al.*, 2008a) both for the first, second and third replicate. It was mixed with carefully measured concentrations of crude oil and then put into the experimental bags.

In the first block, 100, 200, 300, 400 and 500ml of crude oil were introduced to the soil in the experimental bags except in the control. The same process was repeated on the second and third block respectively. The polluted and unpolluted soils were allowed to stand for 1 month (30 days) before amendment was applied. Thereafter, carefully weighed (in grams and mills) *Termiinalia catappa* (leaf litter) and Hydrogen peroxide (H_20_2) were introduced to the treatments except the control. During this period, the soil samples were watered occasionally.

Amendment Materials and Treatment

The following materials were used as remediation agents: leaf litter and hydrogen peroxide. The experiment was in 3 blocks for each plant. Block 1; 10kg of soil was used with 100, 200, 300, 400 and 500ml of crude oil amended with leaf litter (100,200,300,400,500g) and hydrogen peroxide (100,200,300,400 and 500ml) with some unpolluted soils that served as the control. The same experiment was replicated for block 2 and 3 respectively.

Levels of crude oil pollution and amendments with organic and inorganic fertilizers on phaseolus vulgaris, cucumis sativus and solanum melongena

T1	100ml crude oil + 100ml H_20_2
T2	100ml crude oil + 100g leaf litter
T3	200ml crude oil + 200ml H_20_2
T4	200ml crude oil + 200g leaf litter
T5	300ml crude oil + 300ml H_20_2
T6	300ml crude oil + 300g leaf litter
T7	400ml crude oil + 400ml H_20_2
T8	400ml crude oil + 400g leaf litter
T9	500ml crude oil + 500ml H_20_2
T10	500ml crude oil + 500g leaf litter
T11	NO POLLUTION + 500ml H_20_2
T12	NO POLLUTION + 500ml leaf litter
T13	500ml crude oil + NO AMENDMENT
T14	CONTROL

Determination of Nutrient Element Content and Heavy Metals in Plants and soil (Copper, Lead and Zinc) by Digestion method

Total nutrient cation contents of plants gotten by complete oxidation of samples using Kjedahl procedures followed by spectrometric analysis. Either a flame photometer or atomic absorption spectrophotometer may be put into use.

Reagents

1) 62% Per-chloric acid
2) 5ml Nitric acid (concentrated).

Digestion

The International Institute of Tropical Agriculture (IITA) mixed acid digestion method (1979) was adopted. The plant shoots and roots sent for the assertion of heavy metals were digested in the laboratory as follows:

Procedure

One gram (1g) of the plant shoots and roots were weighed into different sterilized 50ml beakers for the respective treatments. 1ml of about 62% Per-chloric acid and 5ml of concentrated Nitric acid was added and the beakers were heated until fuming seized. After 15mins, the heating was stopped following the disappearance of the charred particles.

Health Risk Assessment

Risk Assessment

Risk of intake of TPH and THC contaminated garden egg and groundnut to human health will be characterized by Hazard Quotient (HQ). This is a ratio of determined dose to the reference dose (R_fD). The population will pose no risk if the ratio is less than 1 and if the ratio is equal or greater than 1 then population will experience health risk. This risk

Licensed Under Creative Commons Attribution CC BY

assessment method has been used by researchers (Sridhara C. *et al*., 2008, Chien, L.C. *et al*, 2002, Wang, X., T. et al. 2005) and proved to be valid and true. The following equation will be used;

$$HQ = [W_{plant}] \times [PH_{plant}] / R_fD \times B$$

Where $[W_{plant}]$ will be the weight of contaminated garden egg and groundnut material consumed (mgd^{-1}), $[PH_{plant}]$ will be the concentration of TPH and THC in the plants (*Phaseolus vulgaris* and *Solanum melongena*) ($mg\ kg^{-1}$), R_fD will be the food reference dose for the TPH and THC (mgd^{-1}), and B will be the body mass (kg). The values of R_fD for TPH and THC will be taken from Integrated Risk Information System (Abdollatif G.A. *et al.*, 2009) and Department of Environment, Food and Rural Affair (DEFRA 1999).

Calculation of Estimated Daily Intake

EDI = (C x IR x EF x ED) / (BW x AT)

Where:

C = Mean trace metal concentration in vegetables

IR = the ingestion rate = 300g/day

(Root vegetables) = 0.300kg per day

EF = Exposure frequency (365 days per year)

ED = Exposure duration over a life time (54 years)

(World Bank, 2015)

BW = Body weight (70kg for adults)

AT = Average life time (54 years x 365 days per year)

THQ = Target Hazard Quotient

= EDI/RFD

RFD = Cu = 0.040, Zn = 0.300, Pb = 0.0035

HI = Hazardous Index

HI = $EHQ = HQ_m, + HQ_{m2} + \ldots\ldots$

The conversion factor of 0.085 is to convert fresh garden and groundnut weight to dry weight (Rattan, R.K. *et al*., 2002).

Health Risk Index (HRI):

By using Daily Intake of Petroleum Hydrocarbons (DIPH) and reference oral dose we will be able to obtain the health risk index. The following formula will be used for the calculation of HRI.

$$HRI = DIPH / R_fD$$

If the value of HRI is less than 1 then the exposed population is said to be safe (IRIS. 2003, Yang, T and Lui, J. 2012).

Statistical/Data Analysis

The data collected was subjected to analysis of variance (ANOVA). The means were separated using Least Significant difference (LSD) at 5 % level of probability. The statistical tool employed was Duncan Multiple Range Test (DMRT) (Eckman, S. 2018). It is a post hoc test to measure specific differences between pairs of means.

3. Results

Heavy Metal Concentrations

The evaluation of soils for the concentration levels of toxic elements is essential for healthy crop production, thus this study has endeavoured to determine the levels of Pb, Cu and Zn in the various soil samples. The distribution of mean concentration ± standard deviation of the metals present in the soils is shown in the results below. The results are collaborated by Al-Turli and Helal (2004) and Ren *et al.*, (2005) who reported that lead and cadmium are anthropogenic metals, and without external interferences, are normally not abundant in upper layer soils.

Effect of Treatments On Soil Copper (mg/kg)

An analysis was carried out on the total hydrocarbon content of the soil at the start of the experiment, on pollution, 1 month after amendment, 2 months after amendment, 3 months after amendment, 4 months after amendment and after harvest. From the results as shown below, copper increased on all the polluted and amended soils after pollution (16.4-22.0) which was above the normal range (10mg/kg) set by WHO (1996). T11, T12 and T14 (unpolluted and amended soils and control) was slightly higher than the normal range (11.0-12.0). There was a constant declination on all the petroleum hydrocarbon polluted soils following remediation with organic and inorganic manure.

From the result shown below, the final values at 4 months after remediation were significantly different from the other months having lower values (11.0-12.3) respectively. T13 had the highest copper values on all the months with no much significant difference (20.0-22.0), while the lowest copper values were seen T11, T12 and T14 (4.0, 3.3 and 9.0) four months after amendment.

The final result shows that the introduction of these amendments greatly reduced the copper in the soil up to a level that will not be hazardous to both the soil and the plant.

Licensed Under Creative Commons Attribution CC BY

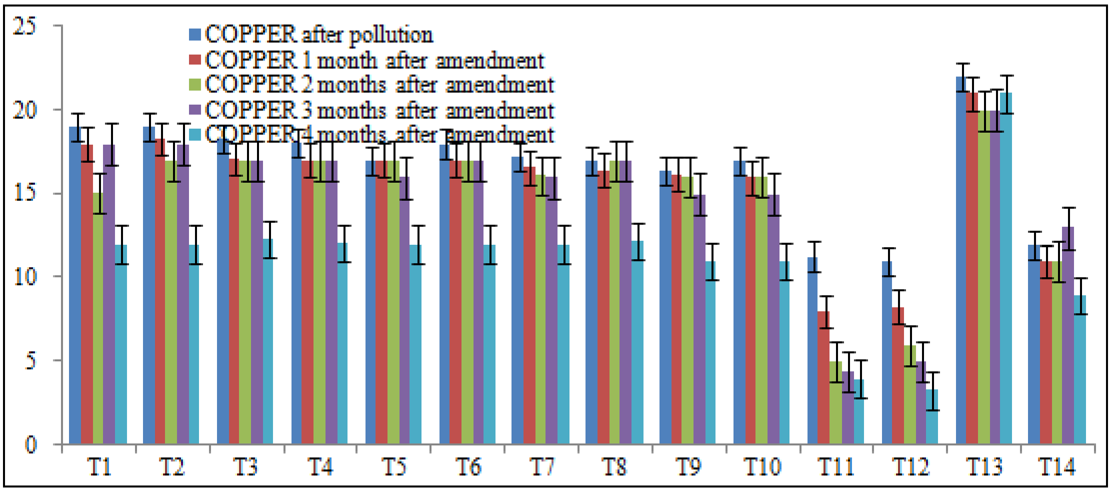

Figure 1: Effects of organic and inorganic manure on soil copper polluted with crude oil**.** T1 = (100ml crude oil + 100ml H_20_2), T2 = (100ml crude oil + 100g leaf litter), T3 = (200ml crude oil + 200ml H_20_2), T4 = (200ml crude oil + 200g leaf litter), T5 = (300ml crude oil + 300ml H_20_2), T6 = (300ml crude oil + 300g leaf litter), T7 = (400ml crude oil + 400ml H_20_2), T8 = (400ml crude oil + 400g leaf litter), T9 = (500ml crude oil + 500ml H_20_2), T10 = (500ml crude oil + 500g leaf litter), T11 = (no pollution + 500ml H_20_2), T12 = (no pollution + 500g leaf litter), T13 = (500ml crude oil + no amendment), T14 = (control)

Effect of Treatments on Soil Lead (mg/kg)

An analysis was carried out on the lead content of the soil at the start of the experiment, on pollution, 1 month after amendment, 2 months after amendment, 3 months after amendment, 4 months after amendment and after harvest.

Lead is naturally present in all soils. It generally occurs in the range of 15 to 40 parts lead per million parts of soil (ppm), or 15 to 40 milligrams lead per kilogram of soil (mg/kg) (U.S.E.P.A. 2001) or 85mg/kg (WHO 1996). From the results as shown below, there was an increase in lead content on pollution on all the treatments (70.3-97.6) with crude oil pollution which was above the acceptable limit set by U.S.E.P.A. there was significant differences in the values on all the months after amendment on the polluted and amended soils. T11, T12 and T14 which were not polluted had low values of lead content (10.04-28.04) below the acceptable limit set by U.S.E.P.A (2001) and therefore safe for planting of crops.

From the result shown below, there were obvious significant differences in values between month 1 and month 4 which was as a result of the effect of organic and inorganic amendments that degraded the lead in the soil up to levels that were acceptable in some of the treatments (T1=40.1, T6=39.2, T7=33.2).

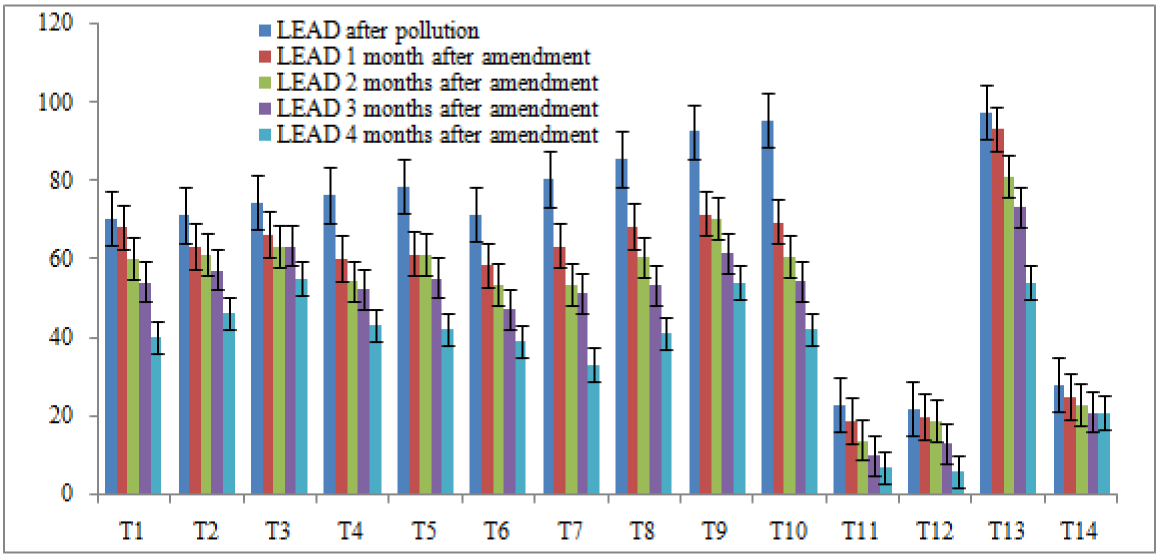

Figure 2: Effects of organic and inorganic manure on soil lead polluted with crude oil**.** T1 = (100ml crude oil + 100ml H_20_2), T2 = (100ml crude oil + 100g leaf litter), T3 = (200ml crude oil + 200ml H_20_2), T4 = (200ml crude oil + 200g leaf litter), T5 = (300ml crude oil + 300ml H_20_2), T6 = (300ml crude oil + 300g leaf litter), T7 = (400ml crude oil + 400ml H_20_2), T8 = (400ml crude oil + 400g leaf litter), T9 = (500ml crude oil + 500ml H_20_2), T10 = (500ml crude oil + 500g leaf litter), T11 = (no pollution + 500ml H_20_2), T12 = (no pollution + 500g leaf litter), T13 = (500ml crude oil + no amendment), T14 = (control)

Licensed Under Creative Commons Attribution CC BY

Effect of Treatments on Soil Zinc (mg/kg)

An analysis was carried out on the zinc content of the soil at the start of the experiment, on pollution, 1 month after amendment, 2 months after amendment, 3 months after amendment, 4 months after amendment and after harvest. From the results as shown below, zinc recorded high values (25.0-32.1) on all the treatment with crude oil pollution on pollution, 1^{st}, 2^{nd} and 3^{rd}month after amendment which subsequently reduced after 4 month of amendment to values between the ranges of (0.1-3.5). T13 which was densely polluted without any amendment had the highest values of zinc on month 1, 2 and 3 which subsequently reduced on month 4 as a result of natural attenuation.

The unpolluted and amended soils and the control soils had the lowest values of zinc on all the months (0.1-9.0) which was below the acceptable limit set by WHO (1996).

From the result shown below, zinc concentration had an obvious significant difference between the 1^{st} month and last month after amendment which is an implication that both leaf litter and hydrogen peroxide degraded the zinc content in the soil to to a limit that will not be harmful to the plant.

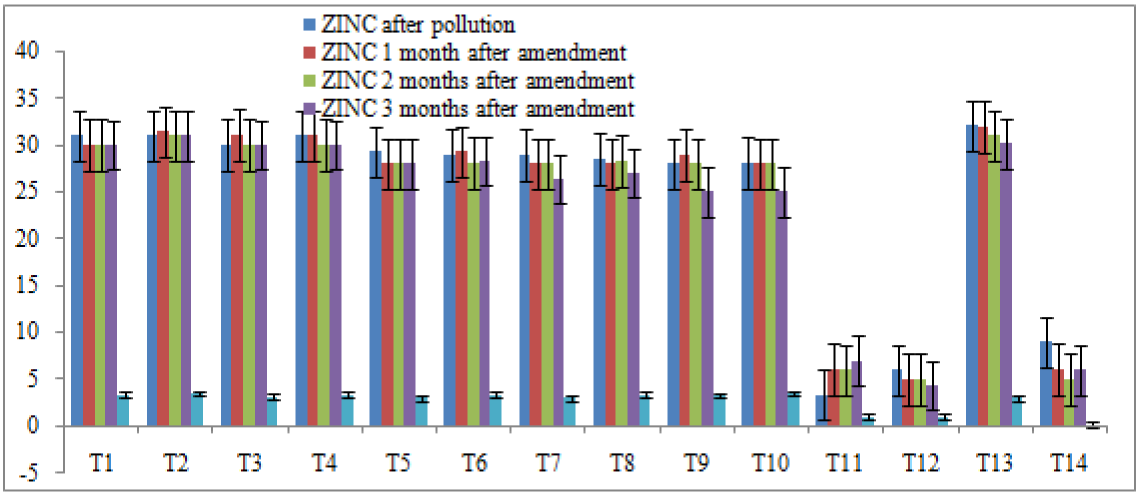

Figure 3: Effects of organic and inorganic manure on soil zinc polluted with crude oil**.** T1 = (100ml crude oil + 100ml H_20_2), T2 = (100ml crude oil + 100g leaf litter), T3 = (200ml crude oil + 200ml H_20_2), T4 = (200ml crude oil + 200g leaf litter), T5 = (300ml crude oil + 300ml H_20_2), T6 = (300ml crude oil + 300g leaf litter), T7 = (400ml crude oil + 400ml H_20_2), T8 = (400ml crude oil + 400g leaf litter), T9 = (500ml crude oil + 500ml H_20_2), T10 = (500ml crude oil + 500g leaf litter), T11 = (no pollution + 500ml H_20_2), T12 = (no pollution + 500g leaf litter), T13 = (500ml crude oil + no amendment), T14 = (control)

Results for Health Risk Assessment

Table 4.17.1, 4.17.2 and 4.17.3 summarizes the health risk assessment in harvested garden egg, cucumber and bean pods from soil polluted with crude oil and remediated with leaf litter and hydrogen peroxide.

The non-carcinogenic risk values of adults in the contaminated and control soils were calculated according to the consumption of these fruits and the heavy metal concentration in vegetables.

The total hazardous index (HI) of the three heavy metals for adults in the polluted, polluted and remediated and control area ranged from 0.003-0.10. The total HI calculated in the samples were <1 which implies that neither of the fruits has no trace of heavy metals and therefore safe for consumption.T61-T65 (polluted and unamended soils) had HI values of 1.54-1.55 which is >1; this implies that bean pods planted on crude oil polluted soils without amendments are not safe for consumption; hence they pose a health risk to humans.

The results below shows that leaf litter and hydrogen peroxide amendments helped in remediating the soil from hazardous metals as shown in the bean pods and hence every plant has a phloem (plant sink) which is the site where assimilates (heavy metals) are stored, the fruits will have no trace of heavy metals and will therefore be safe for consumption (Alonso-Blanco, *et al.*, 2009, El-Lithy, *et al.*, 2004).

Results for health risk assessment of harvested fruits

Beans Pods

	Cu	Zn	Pb	HI
T1-T25 THQ	2.57×10^{-03} 6.425×10^{-04}	8.57×10^{-04} 2.856×10^{-03}	4.28×10^{-05} 0.01	0.01
T1-T25 THQ	2.57×10^{-03} 6.425×10^{-04}	8.57×10^{-04} 2.856×10^{-03}	4.28×10^{-05} 0.01	0.01
T25-50	2.61×10^{-03} 0.065	9.42×10^{-04} 3.142×10^{-03}	4.28×10^{-05} 0.01	0.07
T25-T50	2.61×10^{-03} 0.065	9.42×10^{-04} 3.142×10^{-03}	4.28×10^{-05} 0.01	0.07
T51-T55	2.57×10^{-03} 6.425×10^{-04}	9.42×10^{-04} 3.142×10^{-03}	4.28×10^{-05} 0.01	0.01
T51-T55	2.57×10^{-03} 6.425×10^{-04}	1.07×10^{-03} 3.571×10^{-03}	4.28×10^{-05} 0.01	0.01
T56-T60	2.61×10^{-03} 0.065	9.85×10^{-04} 3.285×10^{-03}	4.28×10^{-05} 0.01	0.08
T56-T60	2.61×10^{-03} 0.065	9.85×10^{-04} 3.285×10^{-03}	4.28×10^{-05} 0.01	0.08
T61-T65 THQ	0.048 1.22	0.013 0.03	1.07×10^{-03} 0.305	1.55

Licensed Under Creative Commons Attribution CC BY

T61-T65 THQ	0.048 1.22	0.013 0.03	1.03×10^{-03} 0.29	1.54
T66	3.21×10^{-03} 0.08	1.07×10^{-03} 3.57×10^{-03}	8.57×10^{-05} 0.02	0.10
T66	3.21×10^{-03} 0.08	1.07×10^{-03} 3.57×10^{-03}	8.57×10^{-05} 0.02	0.10

Results for Health Risk Assessment of Harvested Fruits

Cucumber Fruit

	Cu	Zn	Pb	HI
T56-T60	4.28×10^{-05} 1.07×10^{-03}	8.57×10^{-05} 2.85×10^{-04}	4.28×10^{-06} 1.22×10^{-03}	2.57×10^{-03}
T56-T60	4.28×10^{-05} 1.07×10^{-03}	8.57×10^{-05} 2.85×10^{-04}	4.28×10^{-06} 1.22×10^{-03}	2.57×10^{-03}

Results for health risk assessment of harvested fruits

Garden Egg

	Cu	Zn	Pb	HI
T56-T60 THQ	5.57×10^{-05} 2.14×10^{-03}	1.28×10^{-04} 4.26×10^{-04}	1.28×10^{-06} 3.65×10^{-03}	6.22×10^{-03}
T56-T60 THQ	8.57×10^{-05} 2.14×10^{-03}	1.28×10^{-04} 4.26×10^{-04}	1.28×10^{-05} 3.65×10^{-03}	6.22×10^{-03}

$HQ = \geq 1 \Rightarrow$ Risk associated with consumption.
$HQ = \leq 1 \Rightarrow$ No risk.

4. Discussion

Soil Heavy Metal Content (Zn, Pb and Cu)

Zinc is an essential plant micronutrient. It is important for production of plant growth hormones and proteins and is involved in sugar consumption. Maintaining adequate zinc levels is important for enabling plants to withstand low air temperatures. Zinc is also involved in the synthesis of auxin, a plant hormone that helps plants determine whether to focus on growing tall or becoming bushy (Wade, 2017). Wade (2017) also reported that zinc toxicity is most common when plants are grown in acidic soils and when there is excess magnesium in the soil.

The result showed that on pollution, zinc levels which were deficient in the soils increased to a standard limit and the crops were able to absorb them for beneficial purposes. W.H.O (1996) reported that the standard level of zinc in soil is 50mg/kg which was ideal for planting of agricultural crops. Crops will not achieve their full yield potential and will exhibit stunted growth if their supply of Zn is inadequate. Visual symptoms include short internodes (in cereals) and small leaves; resetting and whirling of (tree) leaves (Brennan and Bolland, 2002).

In summary; the soil zinc increased up to an acceptable level upon the addition of amendments (leaf litter and hydrogen peroxide) when compared to the unpolluted soils in the experiment.

Lead is a heavy metal and often occurs naturally in the soil in concentrations ranging from 10-50 mg/kg (U.S.E.P.A. 2001). Therefore values beyond this limit will pose a great threat to the soil, plant life and even humans through the consumption of such plants.

The result showed that lead (Pb) content increased on pollution with crude oil beyond an acceptable limit in the soil which will be hazardous to plants and living organisms, but upon introduction of leaf litter and hydrogen peroxide amendments, the values of lead decreased in both treatments to values that were significantly lower than the initial values gotten after pollution. The decrease was more evident in the unpolluted and amended soils (T11 and T12) than that of the polluted soils with amendment and the control.

Also, from the result, a great decrease was observed in the copper (Cu) content in the whole treatment after harvest as compared to the initial values gotten on pollution. Soils without pollution and amendment had the lowest copper content in the whole experiment which was lower than that of the control (T14). Sillanpaa, (1982) noted that copper acts as electron carriers in the enzyme systems that brings about oxidation reduction reactions in plants and that such reactions are essential steps in photosynthesis, respiration and many other metabolic processes. In conclusion; simply put that upon the introduction of leaf litter and hydrogen peroxide, the lead and copper content was greatly reduced. Copper and lead content reduction could also have been as a result of plant uptake of these elements.

Health Risk Assessment

Compared with inhalation and dermal contact exposure, food consumption has been identified as the major pathway (Li, *et al.*, 2012). Yang, *et al.*, (2010) reported that vegetable (cucumber and garden egg) is the staple food for much of the world and plays an important role in human diets. Sharma, *et al* (2008) reported that a number of studies have shown heavy metals as important contaminants of the vegetables. Vegetables take up heavy metals and accumulate them in their edible and inedible parts in quantities high enough to cause clinical problems both to animal and human beings consuming these metal-rich plants. Arora, *et al.*, (2008) reported that a number of serious health problems can develop as a result of excessive uptake of dietary heavy metals.

The result for health risk showed that the harvested fruits had no trace of lead, zinc and copper in the polluted and remediated and unpolluted soils (< 1) and are therefore safe for consumption. While that of the polluted soils without amendment showed traces of heavy metals in them (> 1) and are therefore not safe for consumption.Similar result was also observed for Cd in Kidu *et al*, (2015). There was practically no risk assessment in the garden egg and cucumber fruits because there was no yield observed in the polluted soils, but was observed in the unpolluted and remediated soils which showed a health risk index of < 1 which indicates that it is safe for consumption.

5. Conclusion

Heavy metal containing soils may change the physical, chemical and biological properties of the plant. These metals uptake by plants from the soil, it reduces the crop productivity by inhibiting physiological metabolism. Heavy metals uptake by plants and successive accumulation in human tissues and biomagnifications through the food chain

Licensed Under Creative Commons Attribution CC BY

causes both human health and environmental concerns. Appropriate measures should be taken to effectively control heavy metal levels in agricultural soils, and thus protect human health hence they are major consumers of these crops. Excessive accumulation of heavy metals in agricultural soils may not only result in environmental contamination, but lead to elevated heavy metal uptake by crops, which may affect food quality and safety. There is also an increasing concern regarding food safety due to environmental pollution. The HRI value of ＞1 indicated a relative health risk through the consumption of these fruits on polluted soils without any amendment. While HRI of ＜ 1 which was observed on all the polluted soils with amendment (organic and inorganic) indicated safe consumption of these fruits, thus implied that the use of these amendments greatly degraded the petroleum hydrocarbons in the soil up to a limit that was not capable of causing harm to the yield.

Leaf litter as bioremediator is ecologically friendly, easily degraded and doesn't affect humans adversely. It is therefore a better option when compared to hydrogen peroxide which constitutes serious health hazard to man

References

[1] Abdollatif, G. A., Ardalan, M.T., Mohammadi, H.M., Hosseni and Karimian, N. (2009). Solubility test in some phosphate rocks and their potential for direct application in soil. *World Appl. Sci. J.*, 6(2): 182-190.

[2] Alonso-Blanco, C., Aarts, M.G., Bentsink, L., Keurentjes, J.J., Reymond, M., Vreugdenhil, D. and Koornneef, M. (2009). What has natural variation thaught us about plant development physiology, and adaptation? *Plant Cell* 21:1877-1896.

[3] Al-Turki, A.I. and Helal, M.I.D. (2004). Mobilization of Pb, Zn, Cu and Cd, in polluted soil. *Pakistan Journal of Biological Siences*, 7: 1972-1980.

[4] Arora, M., Kiran, B., Rani, S., Rani, A., Kaur, B. and Mittal, N. (2008). Heavy metal accumulation in vegetables irrigated with water from different sources. *Food Chemistry*, 111(4), 811-815.

[5] Ashraf, R., and Ali, T.A., (2007). Effects of heavy metals on soil microbial community and mung beans seed germination. Pakistan Journals of Botany, 39 (2), 629-636.

[6] Bhattacharyya, P., Chakrabarti, K., Chakraborty, A., Tripathy, S. and Powell, M.A. (2008). Fractionation and bioavailability of Pb in municipal solid waste compost and Pb uptake in rice straw and grain under submerged condition in amended soil. *Geosciences Journal*, 12, (1), 41-45.

[7] Brennan, R.F. and Bolland, M.D.A (2002). Relative effectiveness of soil-applied zinc for four crop species. *Aust. J. Exp. Agric.*, 42, pp. 985-993.

[8] Chien, L.C., Hung, T.C., Chaong, K.Y., Yeh, P.J., Meng and Shieh (2002). Daily intake of TBT, Cu, Zn, Cd and As for fishermen in Taiwan. Sci. Total arsenic, cadmium, chromium, copper, lead, mercury. *Environ.*,285:177-185.

[9] DEFRA (Department of Environment, Food and Rural Affairs). (1999). Total Diet Study-aluminium, arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, tin and zinc. The Stationary Office London.

[10] Eckman, S. (2018). Motivated misreporting in web panels. *Journal of SurveyStatistics and Methodology*, 6(3), 418-430. DOI: 10.1093.

[11] El-Lithy, M.E., Clerkx, E.J., Ruys, G.J., Koornneef, M. and Vreugdenhil, D. (2004). Quantitative trait locus analysis of growth-related traits in a new Arabidopsis recombinant inbred population. Plant Physiol. 135: 444-458.

[12] Henry, J.G; Heinke, G.W. (2005). Environmental Science and Engineering, 2nd ed. Prentice Hall, India, New Delhi 110001, 64-84.

[13] IRIS. Integrated Risk Information System (2003). China vis consumption of vegetables and fish. Science Database, US Environmental Protection Agency, USA.

[14] Jordao, C.P., Nascentes, C.C., Cecon, P.R., Fontes, R.L.F. and Periera, J.L. (2006). Heavy metal availability in soil amended with compost urban solid waste. Environmental Monitoring and Assessment. 112, 309-326.

[15] Karaca, A., Cetin, S.C., Turgay, O.C., Kizilkaya, R. (2010). Effects of heavy metals on soil enzyme activities. In: I. Sherameti and A. Varma (Ed), Some Heavy Metals, Soil Biology, Heidelberg 19, pp. 237-265.

[16] Khan, S., Cao, Q., Zheng, Y.M., Huang, Y.Z. and Zhu, Y.G. (2008). Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. Environmental Pollution, 152, 686-692.

[17] Kidu, M., Gebrekidan, A., Hadera, A and Weldegebriel, Y. (2015). Assessement of physici-chemical parameters of Tsaeda Agam River in Mekelle City, Tigray, Ethiopia.

[18] Li, X., Liu, L., Wang, Y., Luo, G., Chen, X., and Yang, X. (2012). Integrated Assessment of Heavy Metal Contamination in Sediments from a Coastal Industrial Basin, NE, China. PloS ONE 7 (6):e39690.doi: 10. 1371/*Journal. Pone.* 0039690.

[19] Ndukwu B.C., Tanee, F.B.G. Obute, G.C. (2012). Understanding Biodiversity and Natural Resources Conservation. Chap. 1, pp.3.

[20] Onuh M.O., Madukwe D.K., Ohia G.U. (2008a). Effects of poultry manure and cow dung on the physical and chemical properties of crude oil polluted soil. *Sci. World J.* 3(2): 45 – 50.

[21] Rattan, R.K., Dutta, S.P., Chandra, S. and Saharaan, N. (2002). Heavy metals in environments-Indianscenario. *Fertil News*, 47:21-40.

[22] Ren, H.M., Wang, J.D. and Zhang, X.L. (2005). Assessment of Soil Lead Exposure in Children in Shenyang, China. *Environ. Pollut.* 144: 327-355.

[23] Sillanpaa, M. (1982) Micronutrients and the nutrient status of soils: A global study. Rome, UN. Food and Agric. Org.

[24] Sharma, R.K., Agrawal, M., and Marshall, F.M. (2008). Heavy metal (Cu, Zn, Cd and Pb) Contamination of vegetables in urban India: A case study in Varanasi. Environ. Pollut., 154: 254-263.

[25] Sridhara, C.N., Kamala, C.T. and Samuel, S.R.D. (2008). Assessing risk of heavy metals from consuming food grown on sewage irrigated soils and food chain

Licensed Under Creative Commons Attribution CC BY

transfer. *Ecotoxicology and Environmental Safety*, 69: 513-524.

[26] Tanee, F.B.G. and D.I. Anyanwu, 2007. Comparative studies of the growth and yield of two cassava lines (TMS 30572 and TMS 30555) in a crude oil polluted habitat. *Scientia Afr*., 6:81-84.

[27] U.S.E.P.A. (2001). "United States Environmental Protection Agency". National-Scale Air Toxics Assessment for 1996. Office of Air Quality Planning and Standards. Research Triangle Park, NC, EPA-453/R-01-003. January.

[28] Wade, T.L. (2017). Review of pollutants in urban road dust and stormwater runoff: part 1. Heavy metals released from vehicles. *Int. J. of Urb. Sci*, 10.

[29] Wang, X., Sato, T., Xing, B. and Tao, S. (2005). Health risks of heavy metals to the general public in Tianjin, China Via Consumption of vegetables and fish. Sci. Database, US Environ. Protec. Agency. *Total Environ.*, 350: 28-37.

[30] World Health Organization (WHO). (1996). *Health Criteria Other Supporting informations in Guidelines for Drinking Water Quality*, Vol. 2, 2nd ed., WHO Geneva; pp. 31-338.

[31] Yang, T. and Liu, J. (2012). Health risk assessement and spatial distribution characteristic of heavy metals pollution in Haihe River Basin. *J. Environ. Anal. Toxicol.* 2:152, DOI: 10.4172/2161-0525.1000152.

Licensed Under Creative Commons Attribution CC BY