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Case Study

How metal concentrations could affect enzyme activities: a case study of a range, near Port Harcourt, Rivers State, Nigeria

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Abstract

Heavy metals released from military exercise and training could affect soil enzyme activity. In this study, five composite soil samples collected near Port Harcourt were analyzed in triplicates for physicochemical properties, heavy metals, and enzyme activities. Data was analyzed to determine the level of contamination and to find out the trend of enzyme activity in the presence of certain heavy metals in the natural environment. Heavy metal pollution index ranged from edge (0.71) to center (1.43) indicating multi-element contamination within the range. Contamination factors showed that cadmium was the most polluting element with a degree of contamination that ranged from edge (35.4) to center (118.7). Lead and copper showed higher values while zinc and copper were only higher than the control. Soil enzymes, dehydrogenase, urease, phenol-oxidase and acid phosphatase showed a negative correlation with heavy metal concentrations. Dehydrogenase with a range of 0.79 - 8.24mg/g dry soil $6h^{-1}$ was the most affected while acid phosphatase, 0.42 - 2.11 µMo – p – nitrophenol was the least affected. Results obtained suggest that the activities of shooting range have a negative effect on soil enzyme activity following decreasing metal concentrations from center to edge.

Keywords: Enzyme activities, Metal contamination, Pollution index, Shooting range.

Introduction

Heavy metals are significant soil pollutants and their toxicity is an increasing problem for ecological, evolutionary, nutritional and developmental reasons[1,2]. Heavy metals here refer to those metals whose specific density are more than 5 g/cm^3 and exert adverse affect on the environment and living organisms[3]. These metals are quintessential to the maintenance of various biochemical and physiological functions in very low concentrations, but become noxious when they exceed certain threshold concentrations. Enzymes are generally referred to as biological catalyst responsible for various biochemical reactions in this case that keep a soil fertile. It is therefore necessary that soil be periodically sampled and analyzed in order to procure more recent information on the state of pollution especially when anthropogenic activities involving release of toxic metals is involved. Activities at any shooting range cause the release of several heavy metals and chemicals into the environment[4]. Detonations of weapons and destruction of expired or contaminated shots and bombs affect the ecological balance of soil biota[5]. Researchers have reported that these chemicals affect adversely the soil flora and fauna[6,7]. Heavy metals can impact on soil ecosystems sufficiently to result in significant losses in quality[8-10]. Their negative impact results from their toxicity to biological processes catalyzed by soil microorganisms. In field studies, contaminated soil have revealed that elevated loading of these heavy metals can result from their toxicity to biological processes catalyzed by soil microorganisms. Field studies of contaminated soil have revealed that elevated loading of these heavy metals can result in diminished microbial biomass, reduced viable bacterial population densities, inhibition of organic mineralization as well as decreased leaf litter decomposition[11-13]. Unlike most organic pollutants heavy metals occur naturally in ore bearing rocks forming soils. Hence, there is a range of normal background concentration of these elements in soil and the environment. A high concentration of these metals is an evidence of pollution except in their ores[14]. Apart from aerosol in the atmosphere and direct effluent discharge into the environment, the concentration of heavy metal is determined by the solubilization release of metals from rock forming materials, adsorption and precipitation reaction which occur in soil and sediments[15]. The extent to which metals are adsorbed depends on the properties of the metal concerned, (degreed hydration, valence, ionic radius and coordination with oxygen) the nature of adsorbent, the physiochemical properties of the environment, the presence of other soluble ligands in the surrounding fluid and other metals present and their concentration[16]. Shooting ranges are areas mapped out from large area and have adjoining boundaries used for other purposes[17]. It is agreed that soil pollutants are often spread to other areas not directly affected by initial pollution process due to rain run offs and flooding. The effect of these range activities could therefore overlap to areas not directly enclosed in the range[18].

In Nigeria shooting range conditions are most often not evaluated as the portion is out of bounds for non soldiers. However, land is convertible; especially when new and larger ranges are acquired overtime the old ones are left for other uses including grazing, cropping etc. As a result of bioaccumulation of heavy metals by plants and adsorption of heavy metal on soil colloids, thus new uses and organisms in old ranges are exposed to the effects of these heavy metals and chemicals. This paper accesses the level of heavy metals pollution in the shooting range near Port Harcourt, Rivers State, Nigeria with a view to find out the trends in effects of metal pollution on the soil enzymatic activities. Researchers have reported various changes in soil enzyme activities due to heavy metals contamination from various anthropogenic sources but similar studies in shooting ranges are scarce[19-22]. Such studies could assist in decision making concerning the soil health and those involved with the area as well as the best use of such areas. Data for future references during monitoring of effects of shooting range activities is also being generated.

Materials and methods

Study area: The study area is the shooting range near Port Harcourt which has served this purpose for well over twenty-five years. It is located South latitude 05^o N in the tropical rainforest region of Nigeria with its characteristic rainforest climate. The rainfall is seasonal, variable and heavy with annual rainfall of about 1.862 mm and the wet season last for at least 9 months. Mean maximum temperature ranges between 28^{o}C to 33^{o}C whereas the mean minimum temperature ranges from 17^{o}C - 24^{o}C. The relative humidity is high throughout the years[23]. This rainforest shooting range has been drastically modified by a lot of human activities. In some areas of the range oil palm and shrubs are found with the chief shrubs in the vegetation being *Chromolena odoratum.* Abura tree, raffia palm, lianas ferns are typical vegetation on this Shooting range. Geology reveals that the shooting range lies on the recent coastal plain of the Eastern Niger- Delta with its surface geology consisting of fluvial sediments. These materials deposited as regolith overburden of 0 – 24 m thickness are clays peat, silts sandy and gravels. The depositional sequence shows massive continental sandstones which overlay an alternation of sandstones and clays of marginal marine origin[24,25]. The land surface around the shooting range and within is mainly the fresh water. It is generally less than 20 m above sea level.

Soil sampling: The entire length of the shooting range was divided into the edge, midway, centre and samples collected, once within the month of February, 2013. Outside the edge (6.6 m away) two samples were collected one from the south and one from north. The control was collected from the same geographical area but well away from the effects of the range activities. At each sampling portion a W-shaped line was drawn on a 2 x 2 m surface from which five samples were collected from a 0 – 24 cm depth. These five portions were pooled, together and treated to coning and quartering until a smaller composite sample was obtained. In each point of the W-shape two auger core portions were taken to make-up one sampling auger. The soil samples were air dried, sieved with a 2 mm mesh size and stored in black polyethylene bags for analysis[26,27].

Physicochemical Analysis: Physicochemical parameters were determined within 1 – 3 days of sample collection except for temperature and pH that were determined *in situ*. Using a mercury bulb thermometer inserted into the soil, the soil temperature was read off after three minutes. This was done same for all nine samples within a period of one hour. Soil pH was determined using a Suntex pH meter Ts – 2 after calibration with buffer of pH 7.0 and pH 4.0. The pH was determined by dipping the electrodes into a 2:1 soil/deionized water that had been stirred and allowed to equilibrate for about an hour[28]. The electrical conductivity (EC) of the soil was determined in µs/cm by use of Yokoguwa conductance Sc. 82 from the suspension used for pH determination. Soil phosphate (PO_4^{-3}), sulphate (SO_4^{-2}) and nitrate (NO_3^-) were determined by the methods stated in UNEP analytical methods for environment[28]. Organic matter content was determined by loss on ignition method using MAC 2000 furnace while moisture content was determined by the weight loss after drying to a constant weight.

Heavy metal analysis: Total heavy metal content of the soil was determined by digestion method. Two grams of each sample was weighed and digested with 20 ml of 4N HNO_3 at 90^{o}C for 4 hours. The digest was filtered into 25ml standard flask and solutions made up to mark with deionized water[29,30]. The concentration of Pb, Cd, Zn and Cu were determined from the respective calibration curves after reading off the absorbance from a 969 Unicam atomic absorption spectrophotometer.

Soil Enzymes Analysis: Soil Enzyme activity for dehydrogenase, urease, phenol oxidase and phosphatases (acid) were determined. Dehydrogenase was determined following a method in which incubation of soil sample with aqueous tiphenyltetrazolium chloride (TTC) at 30^{o}C resulted to Triphynyl formation[31]. The absorbance of Triphenyl formazon was measured at 485nm after methanol extraction and results expressed as TPF^{-1} dry soil 6h^{-1}. Urease activity was determined by colorimetry[32]. This method is based on formation of NH_3-N in urea amended soil samples after 24 hours incubation at 37^{o}C and results was expressed as mg/NH_3-N dry soil 24 h^{-1}. Phenol oxidase was determined according to the method based on the formation of purpuragallin formation in pyrogallic acid amended soil expressed as mg^{-1} dry soil 3h^{-1} [33]. Acid photosphatase activities were determined as described by Tabatabai and Bermear using P-nitrophenylphosphate incubation with soil sample and the result expressed as µmol- P-nitrophenol[34,35].

Data Analysis: Data obtained in this work were subjected to a two tail correlation analysis for soil enzymes activities with heavy metal concentration. Using the standard deviation to test for the differences observed, physiochemical parameters and heavy metal concentration were compared.

Results and discussion

Physicochemical parameters: Various physicochemical parameters of analyzed soil samples are shown in table 1. Soil temperature showed high values at the centre of the shooting ranges as well as samples midway the range. All other areas showed similar soil temperatures. Soil temperature ranged from 27.0 ± 0.21^{o}C to 29.3 ± 34^{o}C. These were higher than the control 26.8 ± 0.16^{o}C.

Soil pH and moisture content showed 15.7 and 18.90 respectively. These follow the same pattern as soil temperatures whereas organic matter, sulphate, phosphate and nitrate followed a gradient with lowest values at the range centre and gradually increased till the edge and outside the range which was quite close to the control.

Organic matter content ranged between 4.22 – 8.37 mg/g, nitrate 0.52 – 3.91mg/g, sulphate 2.12 – 4.82 mg/g and phosphate 16.37 – 29.78mg/g. Physiochemical properties of soil samples suggest adverse effect on soil quality of the shooting range as well. While the most affected areas were slightly acidic with pH 6.21 to 6.87. This is acceptable for crop production [36]. Soil nutrients like PO_4^{3-}, NO_3^- and SO_4^{2-} including organic matter were equally low in these highly contaminated areas. Table 1, shows a general increase in soil nutrients, organic matter, sulphate, phosphate, nitrate, from centre towards range edge with highest values at control. On the other hand the heavy metals show highest concentrations at centre decreasing towards the edge and lowest at control. The trend in electrical conductivity and moisture is not clearly seen as in the case of soil nutrients and heavy metal. There is a high probability of antimineralization and humidification effects on the soil. These are unlike the situation in the control and outside the range. The observations here are in agreement with those in South Korea[37]. Lee equally reported that heavy metal concentrations reduce organic matter as in other researchers[39,40].

Heavy metal concentrations: The concentrations of all four heavy metals studied increased with distance from centre of the range i.e. all four heavy metals had their highest concentration at the center of the shooting range Zn (214.61 mg/kg) >Pd (183.14 mg/kg) > Cu (172.31mg/kg) > Cd (0.97mg/kg). Outside the edge the concentration were closer to that for the control sample. Zinc (Zn) metal had the highest concentrations in the soil sample with a range of 46.1 mg/g followed by lead (Pb) 41.61 mg/kg and copper (Cu) 41.11 mg/kg. Cadmium (Cd) showed lowest concentration of 0.02 mg/kg. Therefore heavy metal concentration showed significant differences with regards to sampling point (Table-2).

These trends were expected and are in agreement with other researches[41]. When compared with the control, the results suggest that shooting range activities were significantly affecting the soil quality. Heavy metals concentrations at the range centre were statistically higher than those of the normal soil. According to the report CEC Directives[42] values of Pb, Cu, Cd, and Zn were too high within the range than values obtained outside fence and control, confirming the observation that shooting range activities are the prime suspect for elevated heavy metal concentrations in soil within the range.

Table-1: Mean values physiochemical parameter of the soil samples.

Parameter	Centre	Midway	Edge	Outside Range	Control
Temperature (^{o}C)	29.3 ± 0.34	29.1 ± 0.41	27.2 ± 0.12	27.0 ± 0.21	26.8 ± 0.61
Ph	6.21 ± 0.41	6.24 ± 0.43	6.87 ± 0.61	7.01 ± 0.40	7.62 ± 0.61
EC (µsm^{-1})	0.62 ± 0.14	0.58 ± 0.10	0.58 ± 0.61	0.60 ± 0.12	0.61 ± 0.12
Moisture (mg/g)	15.7 ± 0.21	16.2 ± 0.27	17.30 ± 40	18.9 ± 0.62	18.31 ± 0.64
OM (mg/g)	4.22 ± 0.31	4.77 ± 0.34	5.71 ± 0.52	6.14 ± 0.80	8.37 ± 0.81
SO_4^{2-} (mg/g)	2.12 ± 0.11	2.92 ± 0.14	3.11 ± 0.52	4.01 ± 0.42	4.82 ± 0.64
PO_4^{3-} (mg/g)	16.37 ± 0.41	17.81 ± 0.47	19.27 ± 0.24	21.43 ± 0.26	29.78 ± 0.67
NO_3^- (mg/g)	0.52 ± 0.11	0.84 ± 0.20	1.20 ± 0.42	2.12 ± 0.61	3.8 ± 0.82

Mean ± SDV for n=3

Heavy metal Pollution index (HMPI): The pollution Index (HMPI) of the soil was estimated by averaging the ratios of metal concentration to assumed permissible levels for each metal divided by the total number of heavy metals analyzed[43]. The expression for HMPI is;

$$HMPI = \frac{[Cd]}{PL} + \frac{[Cu]}{PL} + \frac{[Pb]}{PL} + \frac{[Zn]}{PL}/4 \quad (1)$$

The permissible level (PL) adopted for this studies were the FEPA standards for soils in Western Nigeria. The pollution indices of the various sampling locations were calculated and the mean of centre midway and edge gave HMPI within the shooting range. The heavy metal pollution index followed the same pattern as metal concentrations, as follow: $HMPI_{CE} > HMPI_M > HMPI_E > HMPI_O > HMPI_C$.

The high metal concentrations at the centre and midway the shooting range could be ascribed to activities involving weapon discharge. These weapons contains copper, lead and zinc alloys which add to the concentrations in the soil when release from the weapons[44]. These additions results in the increase above the range edge and control. It was observed that normal activities at any shooting range results in release of heavy metals into the environment as observed in the paper. Rain water runoff may be responsible for the high concentrations of these metals in the sampling point immediately outside the range. It has earlier been reported that similar observations where pollutant concentrations form a gradient away from the point of pollution due to rain water runoffs carrying the release pollutants away from point of pollution[45-47].

Soil enzymatic activities: Table-3 shows values of soil enzymatic activities. Amongst the soil enzyme activities studied dehydrogenase exhibited highest activities ranging from 0.79 – 8.24mg/g dry soil $6h^{-1}$, followed by urease with 0.62 – 3.41 mg/g $24h^{-1}$. Phenol oxidase had activity range of 0.57 – 2.41mg/g dry soil $6h^{-1}$. The least enzyme activity was recorded in acid phosphatase with a range of 0.42 – 2.11mg/g dry soil $3h^{-1}$. All soil enzymes had significantly different enzyme activity values at each sampling point (Table-2). Despite these differences, soil enzymatic activities values correlated strongly and negatively with heavy metal concentrations. Soil samples with high heavy metal concentrations had lower soil enzymatic activities, whereas soil samples with low heavy metal concentrations showed high enzymatic activities.

Table-2: Mean values of heavy metal concentrations and HMPI of soil samples.

Metal symbol	Centre	Midway	Edge	Outside Fence	Control
Cd	0.97 ± 0.11	0.54 ± 0.23	0.21 ± 0.43	0.04 ± 0.64	0.01 ± 0.60
Cu	172.31±0.61	126.54±0.87	107.25±0.91	41.11 ± 1.41	29.54 ± 1.68
Pb	183.14±0.16	163.67±0.20	112.45±0.42	42.31 ± 1.40	20.61 ± 1.62
Zn	214.61±0.11	186.61±0.21	162.42±0.36	46.1 ± 1.20	31.31 ± 1.60
HMPI	1.43	0.95	0.71	0.15	0.12

Mean ± SDV for n=3

Table-3: Mean values of soil enzyme activities with respect to sampling point.

Enzyme	Centre (CE)	Location Midway(M)	Edge (E)	Outside Fence (O)	Control (C)
Dehydrogenase (mg/g dry soil $6h^{-1}$)	0.79 ± 0.21	1.82 ± 0.21	3.60 ± 0.67	6.78 ± 0.88	8.24 ± 0.92
Urease (mg/g dry soil $24h^{-1}$)	0. 62 ± 0.21	0.93 ± 0.40	1.21 ± 0.59	2.42 ± 0.72	3.41 ± 0.96
Acid phosphatase (mg/g dry soil 34^{-1})	0.42 ± 0.22	0.82 ± 0.27	1.21 ± 0.40	1.87 ± 0.61	2.11 ± 0.82
Phenol oxidase (mg/g dry soil $6h^{-1}$)	0.57 ± 0.13	0.72 ± 0.42	1.11 ± 0.67	1.48 ± 0.83	2.41 ± 0.87

Mean ± SDV for n=3

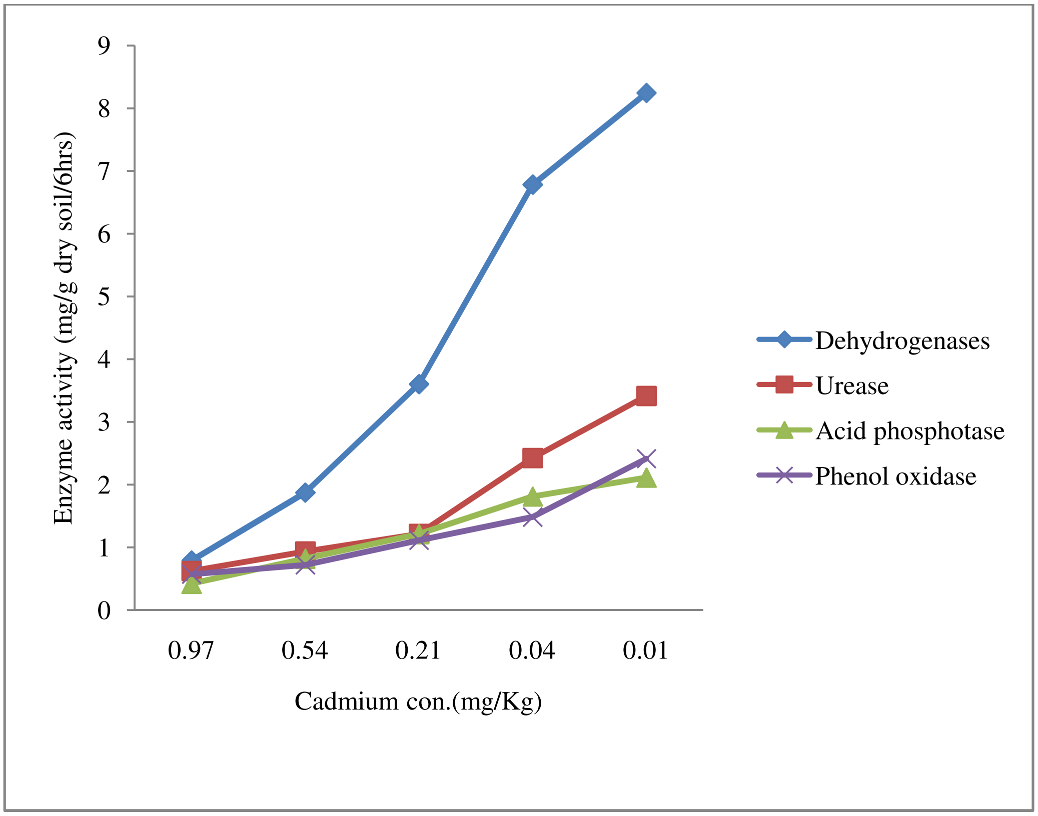

Figure-1: Enzyme activities against dereasing cadmium contcentrations.

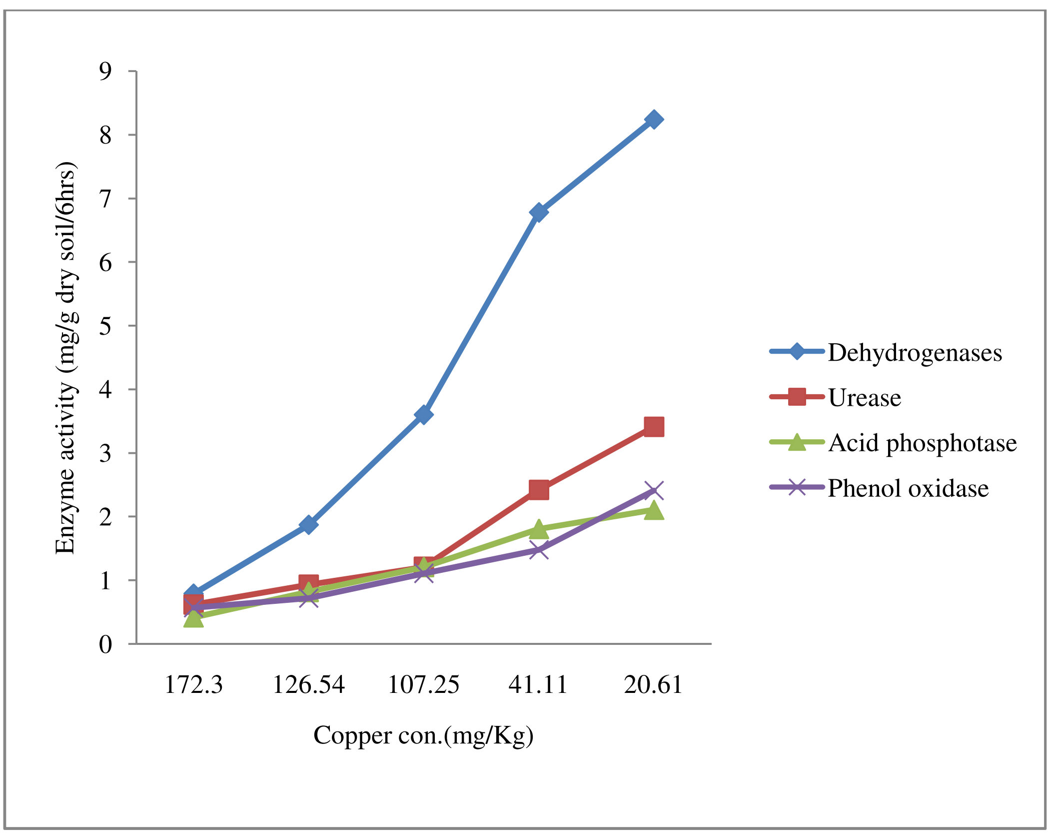

Figure-2: Enzyme activities against dereasing copper contcentrations.

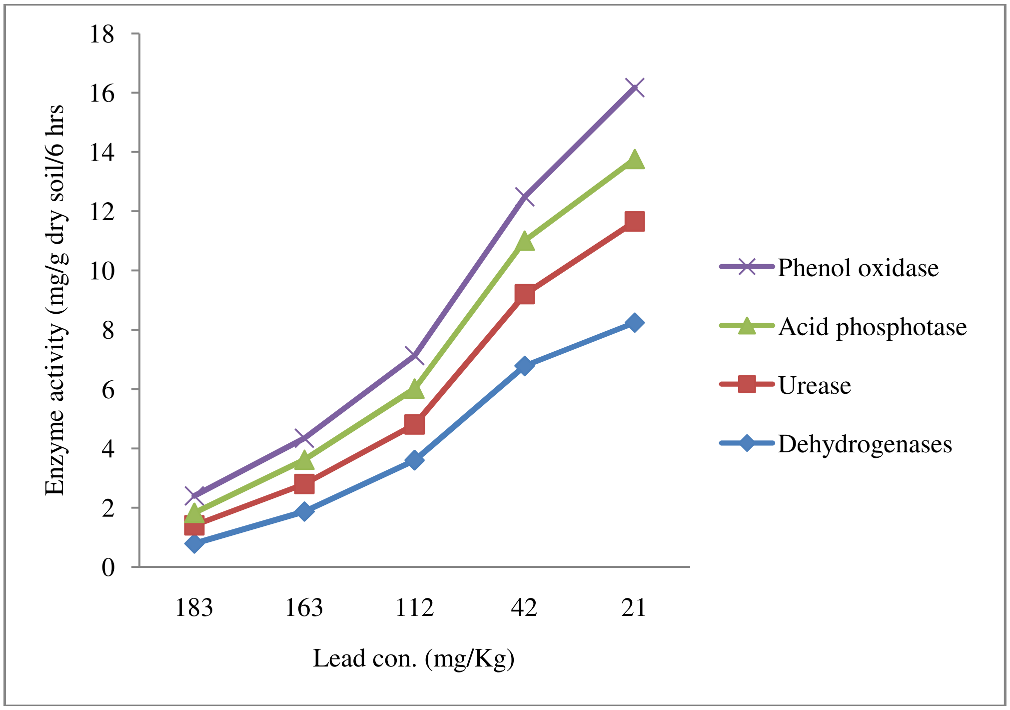

Figure-3: Enzyme activities against dereasing lead contcentrations.

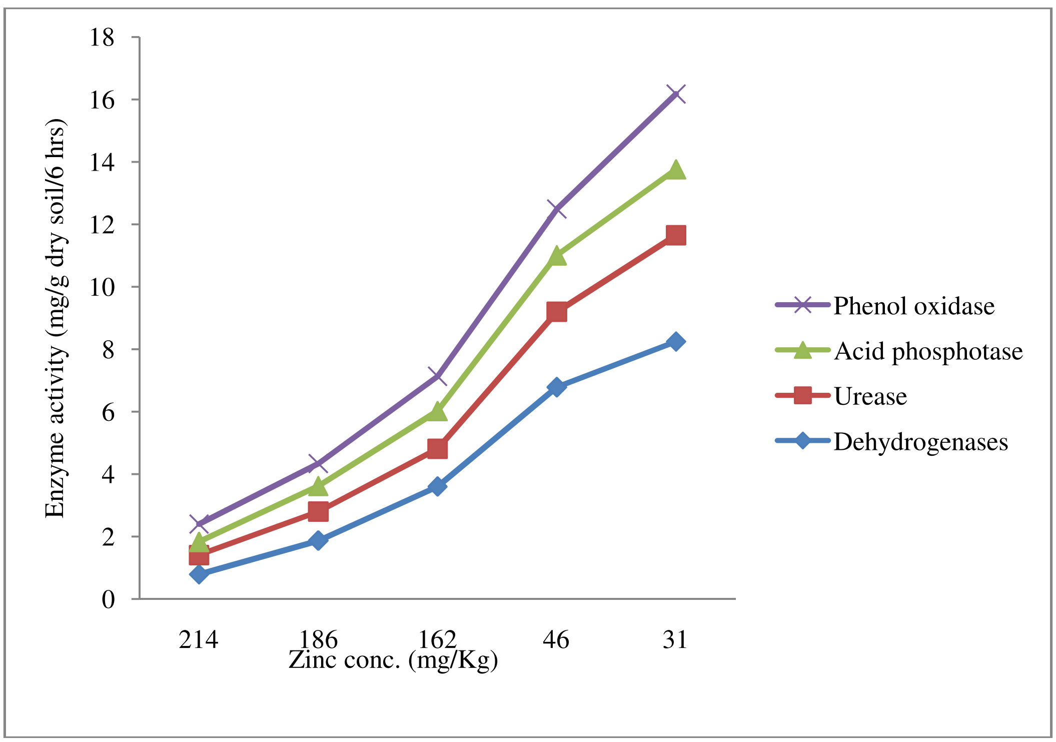

Figure-4: Enzyme activities against dereasing Zinc contcentrations.

Dehydrogenase activity was most affected by cadmium concentration (Figure-1) compared to other soil enzyme activities.With respect to cadmium and copper (Figures-1 and 2) the decreasing trend of soil enzyme activities was as follows; dehydrogenase > urease > acid phosphatase > phenol oxidase.

It was also observed that phenol oxidase activity was the most affected by lead while the least was dehydrogenase activity. The decreasing trend with respect to copper was the same as for zinc as follows: phenol oxidase > acid phosphatase > urease > dehydrogenase. This seems to be a reverse of the trend with cadmium and copper. However Figures-3 and 4 showed that at high metal concentrations acid phosphatase and urease activities had similar values.

Contamination Factors (C_f) and Degree of Contamination (C_d): The contamination of heavy metals in shooting range soils were assessed by use of contamination factors (C_f) and degree of contamination (C_d). The C_f and C_d were calculated as suggested through these formulae[48]:

$$Cf = \frac{Cs}{Cb} \tag{2}$$

Where: C_s is the measured concentration of the examined metal in the shooting range soils while C_b is standard regulatory limits/ background levels of metals in soil reported by many researchers[49-52], with the following concentration in mg/Kg 90, 30, 8 for Zn, Cu and Cd respectively. Lead permissible level for soil was taken as 21.0 mg/Kg according to researchers[53-55].

$$Cd = \sum Cf \tag{3}$$

Metal contamination factors followed the trend as metal concentrations i.e decreasing from centre outwards. For all four metals contamination factors were least at the control ranging from copper (C_f = 1.4) to cadmium (C_f = 4).While cadmium showed highest contamination factors in all samples within the range, it had the least contamination factor for the control. In addition cadmium exhibited the most drastic reduction contamination factors from range centre (97) > midway (54) > edge (21) > outside fence (4) > control (0.001). The insignificant contamination factor for cadmium at control suggest that source of cadmium is strictly from shooting range activities involving cadmium compounds. It was equally observed that center of range was the most contaminated with a degree of contamination of 118.7 and that contribution of cadmium was highest amongst all metals analyzed.

In other to further explore the relationship between metal contamination factors and soil enzyme activities data was plotted to produce Figures-6 to 9. From Figures- 6 to 8 it could be observed that decreasing contamination factors generally favored increasing enzyme activities and since these figures showed marked similarities in trends it was concluded that metal contamination factors affect all soil enzyme activities to the some extend. However a critical look at Figure-6,7 and 8 reveals that contamination factor of cadmium had the highest effect on dehydrogenase, urease and phenol oxidase. In all three cases the order of decreasing effect of contamination factors of soil enzyme activities were Cd>Cu>Pb>Zn.

It was observed that Figure-7 showed a different trend and that cadmium contamination factors showed least effect on soil acid phosphatase activity while other metal contamination factors had approximately same effect. The trend of decreasing effect of metal contamination factors on enzyme activities was Zn > Pb>Cu> Cd and could be seen to be a reverse of the case in Figures-6, 7 and 8.

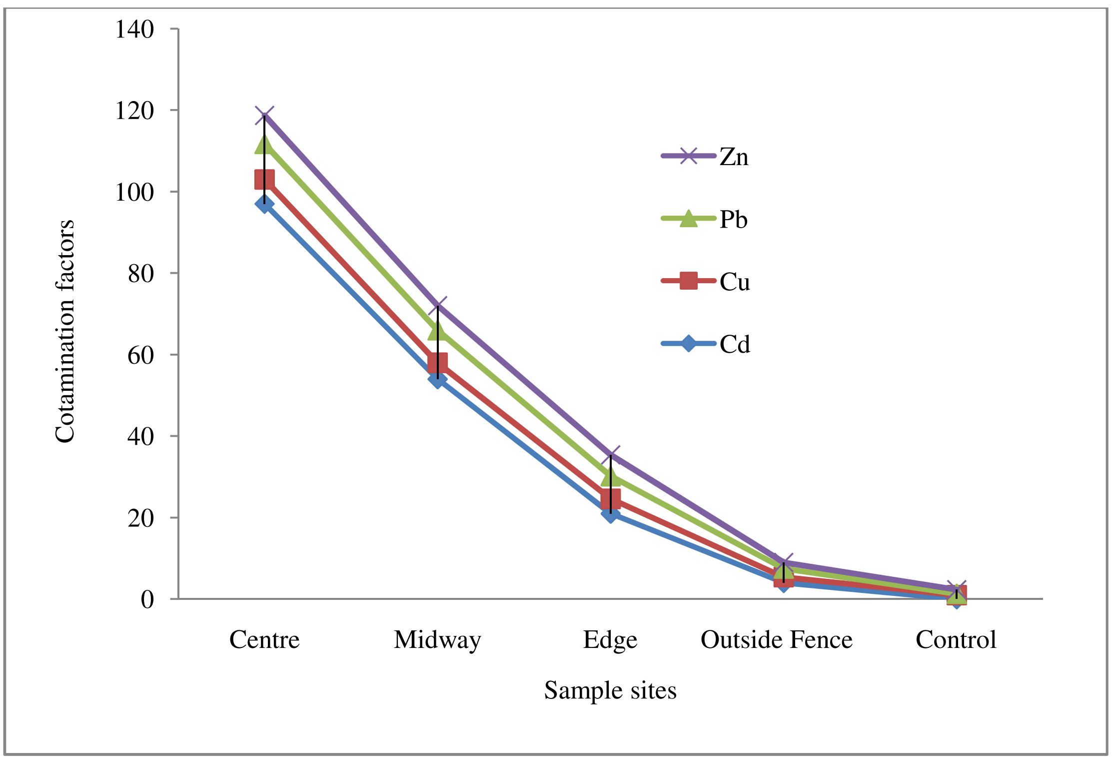

Figure-5: Contamination factors and degrees of contamination.

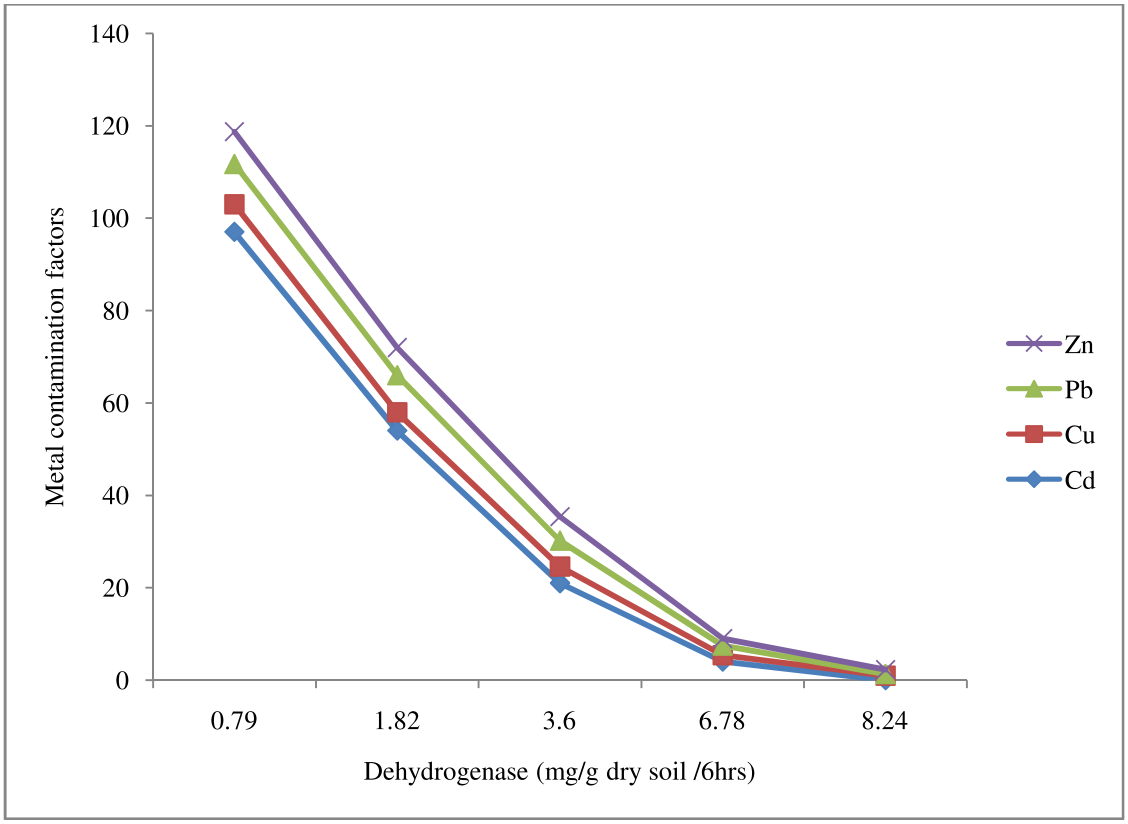

Figure-6: Metals contamination factors against dehydrogenase activity.

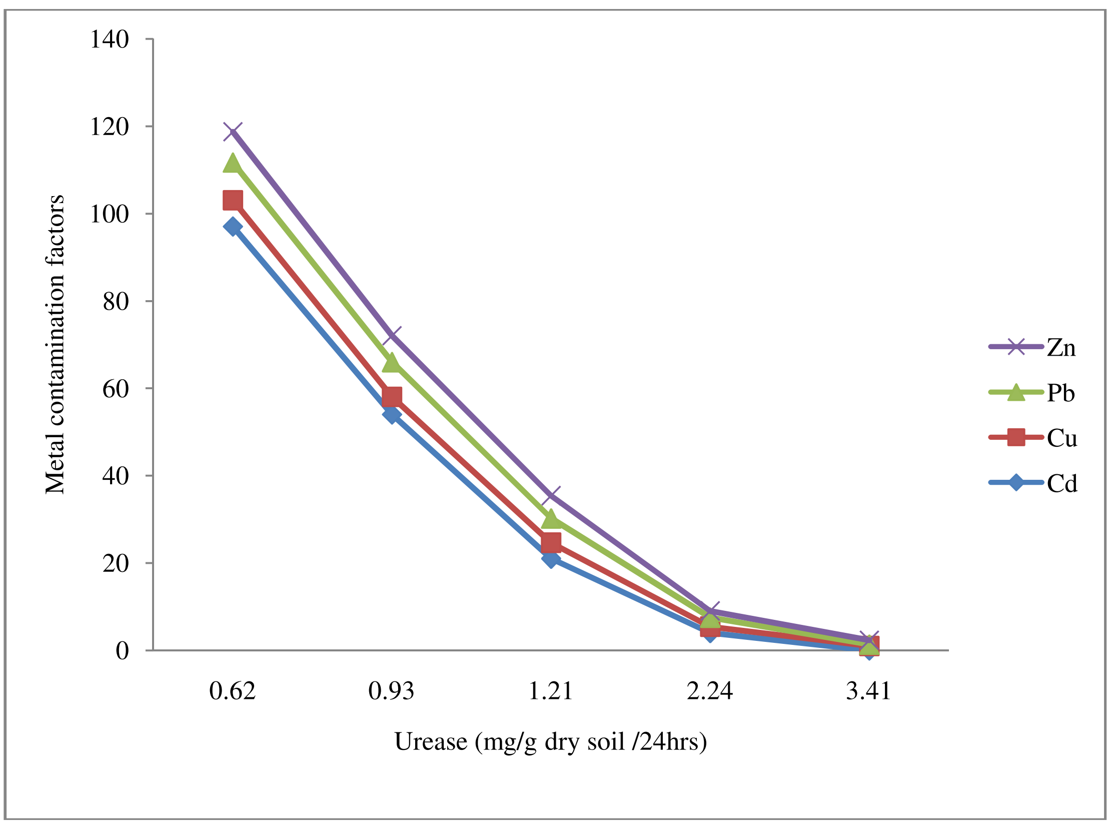

Figure-7: Metals contamination factors against ureaase activity.

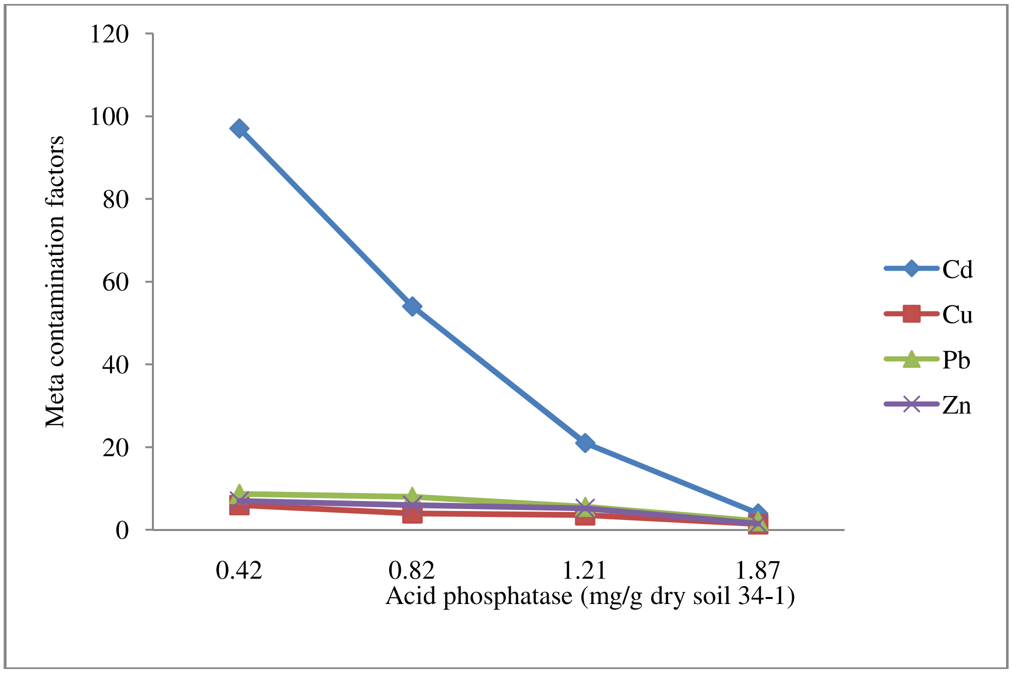

Figure-8: Metals contamination factors against acid phosphatase activity.

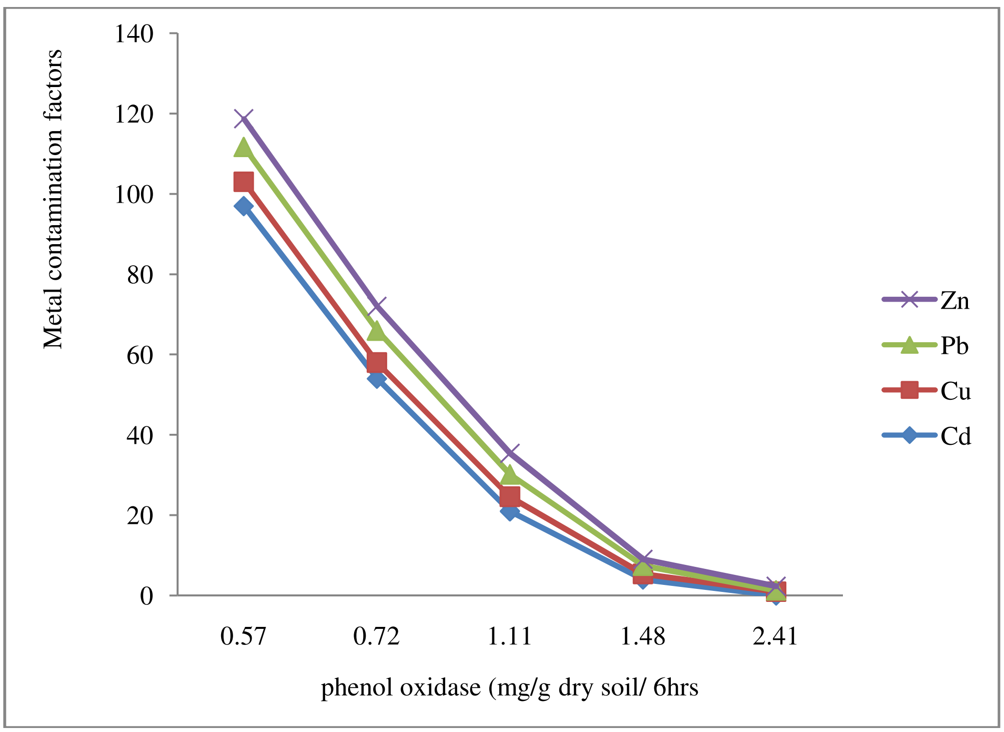

Figure-9: Metals contamination factors against phenol oxidase activity.

This paper therefore ascertains that high levels of heavy metals in soil leads to a reduction in soil nutrient levels including soil moisture and pH. Observation of the enzymatic activities tends to agree with Zhang et al.[56] and Gills et al.[57] in which they stated that heavy metals affect soil enzymes adversely. Heavy metals inhibit the activities of those enzymes including other processes in the microbial species resulting in low enzymatic activities[58].

Though the general trend in increasing metal contamination showed a resulting decrease in soil enzyme activity, the dehydrogenase activity was the most affected by the heavy metal pollution. This work corroborates who proposed that soil dehydrogenase could be used as biological indicator of heavy metals pollution[60].

Table-4: Values of some statistics and equation for linear correlation of Metal-Enzyme.

S/no	Metal-Enzyme	R^2	r-values	Equation for linear correlation	p-value	Remark
1	Cd- Dehydrogenase	-2.06	1.35	$Y = 2.236X$	0.001	Strongly negative
2	Cd- Urease	-1.7	1.303	$Y = 0.694X$	0.000	Strongly negative
3	Cd- Acid phosphotase	-3.58	1.892	$Y = 0938X$	0.001	Strongly negative
4	Cd- Phenol oxidase	-1.92	1.385	$Y = 0.551X$	0.001	Strongly negative
5	Cu- Dehydrogenase	-1.55	1.245	$Y = 0.021X$	0.001	Strongly negative
6	Cu- Urease	-1.31	1.144	$Y = 0.007X$	0.000	Strongly negative
7	Cu- Acid phosphotase	-1.55	1.245	$Y = 0.021X$	0.000	Strongly negative
8	Cu- Phenol oxidase	-2.16	1.497	$Y = 0.007X$	0.001	Strongly negative
9	Pb- Dehydrogenase	-1.66	1.288	$Y = 0.017X$	0.001	Strongly negative
10	Pb – Urease	-1.38	1.175	$Y = 0.006X$	0.000	Strongly negative
11	Pb - Acid phosphotase	-2.67	1.634	$Y = 0.006X$	0.001	Strongly negative
12	Pb - Phenol oxidase	-2.36	1.536	$Y = 0.015X$	0.001	Strongly negative
13	Zn - Dehydrogenase	-1.60	1.265	$Y = 0.005X$	0.000	Strongly negative
14	Zn – Urease	-1.34	1.157	$Y = 0.005X$	0.000	Strongly negative
15	Zn - Acid phosphotase	-2.55	1.597	$Y = 0.005X$	0.001	Strongly negative
16	Zn- Phenol oxidase	-2.24	1.497	$Y = 0.005X$	0.001	Strongly negative

It could be observed that all relationships were negative, i.e the presence of heavy metals have only negative effects on enzymes activity**.** Most correlations between metals and enzymes activity were strongly negative such as Cd - Acid phosphotase (-3.58), Pb - Acid phosphotase (-2.67) Zn- Acid phosphotase (-2.55) while Cu – Urease (1.31) and Zn – Urease (1.34) had weak negative correlations. Ranking these metal – enzymes activity relationship in a decreasing order of effect by metals showed that Cd>Pb>Zn>Cu. All correlations had p-values ranging between $p \geq 0.001$ and $p \leq 0.001$. For p-values less than $p < 0.05$ indicates that the null hypothesis[61] (Hi: the coefficient of correlation is equal to 0). In other words; variable with low p-value have a meaningful addition to the model i.e a change in the metal concentration could a large change in the enzyme reactivity. Therefore, all metal concentrations studied here can bring about large changes (negative) on the enzyme activities.

Conclusion

Shooting range soil near Port Harcourt Nigeria lacks soil nutrients following reduced enzymatic activities. Multi-element contamination as confirmed by heavy metal pollution index was above 1 at centre of range. Soil enzyme activities have been shown to be affected by heavy metal concentrations from shooting range activities. This could be due to metal toxicity. If the area is to be put into other use rehabilitation of the soil must be carried out to avoid risk of heavy metals intoxication of new users. Rehabilitation becomes even very essential in the case of agricultural activities because plants will bioaccumulate these heavy metals in their tissues. Non economic trees that can bioaccumulate these metals could be planted in the shooting range so that the conversion of the land will be easier when the need arises in future.

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