Speciation Distribution of Heavy Metals in Dutsen-Soyaya Shooting Range soil within the Nigerian Army Base Camp, Kachia, Kaduna State, Nigeria

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Abstract: **In soil, heavy metals can be found in large quantities. Anthropogenic activities raise heavy metal concentrations in the soil, which are readily assimilated by food crops. Military training exercises such as shooting in a shooting range with bullets containing a mixture of heavy metals raise the concentration above the baseline over time, affecting military personnel and crops alike negatively. It is critical to determine the effect of shooting via military artillery operations on the soil heavy metal concentrations, mobility, and bioavailability on the shooting range by analyzing soil samples collected from selected areas of the shooting location. The speciation of heavy metals (Copper (Cu), Manganese (Mn), Nickel (Ni), Lead (Pb), Arsenic (As), Chromium (Cr), Cobalt (Co) and Zinc (Zn)) distributed in the Dutsen-Soyaya Shooting range soil within the Nigeria Army Base Camp, Kachia, Kaduna State, Nigeria was investigated. The concentration of these metals after undergoing sequential extraction procedures was analysed using Atomic Absorption Spectrophotometry. The distribution fractions of these metals in the shooting range soil were as follows: Co: Residual > Organic > Fe – Mn Oxide > Bound to carbonate > Exchangeable. As: Fe – Mn Oxide > Residual > Organic > Bound to carbonate > Exchangeable. Cr: Exchangeable > Fe – Mn Oxide > Bound to carbonate > Organic > Residual. Ni: Fe – Mn Oxide > Exchangeable > Bound to carbonate > Residual > Organic. Mn: Residual > Fe – Mn Oxide > Bound to carbonate > Organic > Exchangeable. Pb: Residual > Organic > Fe – Mn Oxide > Exchangeable > Bound to carbonate. Zn: Fe – Mn Oxide > Bound to carbonate > Residual > Organic > Exchangeable. Cu: Residual > Bound to carbonate > Fe – Mn Oxide > Exchangeable > Organic. Although the total concentration of some of these metals (Co, As, Cr, Mn, Pb and Ni) were above the permissible limits by WHO standards, the toxic metals speciation showed that they were mostly predominantly concentrated in the non-bioavailable fractions of the shooting site soils.**

Keywords**: Dusten-Soyaya, Heavy metals, Shooting site and Speciation,**

I. INTRODUCTION

Heavy metals are found naturally in soils, and their original sources are the primary minerals and parent material that make up the earth's crust (Ramzan *et al.*, 2017). Heavy metals in soils are bound in mineral complexes by mechanisms like absorption, ion exchange, co-precipitation, complexation, and soil properties like organic matter, carbonates, and oxides influence their mobility (Kabata-Pendias and Pendias, 2001). Heavy metals are abundant in the environment. The natural source of these metals is extremely limited, and anthropogenic activities are the primary contributor, potentially increasing their concentration in soils. Some of these anthropogenic activities include manufacturing industries, mining and dredging activities (Kumar *et al.*, 2014; Olowu *et al.*, 2015). Military exercises such as artillery firing and warfare training have a negative impact on soil properties. (Guiney *et al.*, 2020). Weapon residues in soil have been reported to release toxic elements such as tin (Sb), lead (Pb), chromium (Cr), arsenic (As), mercury (Hg), nickel (Ni), and cadmium (Cd) during military exercises. (Islam *et al.*, 2016). The soil on shooting ranges contains high concentrations of metals from spent ammunition after years of use. For the years 2002–2010, a mean annual deposition of 48, 68, 6, and 5 metric tons of Pb, Cu, antimony (Sb), and zinc (Zn) in Norwegian military small arms shooting ranges was calculated (Myhre *et al.*, 2013). Pb contamination in shooting range soil has been a major concern ecologically and in the health of human posing as risk for booth shooters and workers (Bai and Zhao, 2020). Metals released during the discharge of firearms include bullet fragments and cartridge casings, which, like GSR, have the potential to enter the surrounding soil and groundwater. Commercial cartridge cases are typically made of brass, but they can also be made of steel or aluminium. Most bullets have a Pb core and can be jacketed (covered in Cu, Ni, brass, steel, or other materials) or unjacketed (solid Pb, possibly hardened with Sb) (Black *et al.*, 2021). Despite the high concentration of metals in military shooting range soils, the majority of these metals are found to be in the non-bioavailable region via speciation. (Nwaedozie *et al.*, 2020).

The data obtained from total metal content is insufficient to assess the impact of metal pollution, as well as the likelihood of metal mobilization and remobilization under various environmental conditions. (Ure, 1993); as uptake and bioaccumulation of heavy metals by plants are usually influenced by its bioavailable forms and interactions (Li *et al.*, 2014). Contaminant mobility and availability in the soil have an impact on their ability to spread in the environment, as well as their uptake and toxicity in organisms (Sanderson *et al.*, 2018). Pb, Cu, Fe, Ni, Mn, and Zn concentrations in the soil were found to be higher, along with lower organic matter content and higher soil density, in a study at a shooting range in Alytus, Lithuania, indicating soil toxicity to the earthworm *E. fetida* (Česynaitė *et al.*, 2021).

Many scholarly articles on heavy metal concentrations in soil depict various concentration values of these metals in industrial or active metallurgical sites without using the sequential extraction technique for total metal concentration or speciation for metal distribution. For example, Cr toxicity is determined by its speciation, which controls metal uptake, transportation, and accumulation (Ertani *et al.*, 2017). The goal of this study is to determine the speciation status of heavy metals released as a result of shooting activities in the soil of the Dutsen-Soyaya shooting range in order to recommend remedial actions. Dutsen-Soyaya shooting range is one of the numerous outdoor shooting ranges used by the Nigerian Defence Academy to train its military personnel. Military warfare training, which includes the use of artillery and explosives, increases the concentration of heavy metals on the shooting range over time. In addition, when the site is not in use, some farmers have been observed using the shooting range for their farming activities. If heavy metals are introduced into the food chain, they accumulate in the bodies of organisms, causing diseases and death over time.

II. MATERIALS AND METHODS

1. Sample Collection and Preparation

Soil samples were taken from the Dutsen-Soyaya Shooting site in Kachia Local Government, Kaduna State, which is part of the Nigerian Army Base Camp military shooting range. Sampling took place in February when there was no military training activity at the sampling site. Within the shooting area, a 1000 meter long transect was marked with a wheeled measuring meter. A soil auger was used to collect surface soil samples from the various sample areas at a surface level (0-30 cm depth). The experimental design entailed collection of samples over a one-month period using a random sampling design, harmonizing the stored samples into two composite samples, analyzing the samples and interpreting the results. Soil samples were collected randomly within the grid at the sampling location, with ten (10) composite samples formed after each sampling period. Within the grid, these composite samples were collected in duplicate and stored in labelled polyethylene bags. After being air-dried, ground with a mortar and pestle, and sieved with a 1mm sieve into coarse and fine fraction sand, each stored sample was thoroughly homogenized at the end of the sampling period. It was then placed in a plastic container to be analyzed (Nwaedozie *et al.*, 2020).

2. Soil pH determination

In two 250 cm^3 beakers, 20 g of sample soil was weighed in duplicate. The first and second beakers each received 50 cm^3 of distilled water. The second set of beakers containing the soil solution received 150 cm^3 of 0.01 m $CaCl_2$, and the two sets of beakers were stirred for 1 minute before being left to stand for 15 minutes. The mixture was stirred once more before being left for another 15 minutes. The pH meter was calibrated using different pH buffer solutions of pH 4, 7, and 9 while waiting for the last 15 minutes. The electrode of the pH meter was inserted into the supernatant liquid after the last 15 minutes to read the pH values. The pH of both water and calcium chloride was calculated (Joan, 1999).

3. Total Metal Content

To prevent loss by spattering during digestion, 2g of soil sample was weighed in a 250cm^3 beaker and moistened with a few drops of deionized water. The soil samples were digested on a hotplate (Ohaus Mini hotplate HSMNHS4CAL) in a fume cupboard with 10 cm^3 of concentrated HNO_3 until the volume was reduced to 3cm^3. The residue was then heated for 10 minutes in a mixture of concentrated acids containing 5cm^3 of concentrated HCl, HNO_3, and $HClO_4$ each, until the final volume of the solution was about 5 cm^3. The digest was then allowed to cool before being filtered through Whatman No.40 filter paper into a 100 cm^3 volumetric flask and made up to the mark with distilled water. Then it was then transferred to a plastic sample bottles and analysed with an Atomic Absorption Spectrophotometer (Thermo Scientific Model: iCE 3000 v1.30) for metal content concentrations such as Arsenic (As), Lead (Pb), Cobalt (Co), Manganese (Mn), Copper (Cu), Nickel (Ni) and Zinc (Zn) (Majolagbe *et al.*, 2013).

4. Sequential Chemical Extraction of Metals

The distribution of heavy metals in various fractions such as Exchangeable fractions (F1), Carbonate fractions (F2), Easily reducible fraction (F3), Organic fraction (F4) and Residual Fraction (F5) of the soil samples in the sampled location was determined using sequential extraction method (Tessier *et al.*, (1979); Nwaedozie *et al.*, 2020).

5. Mobility Factor

The mobility factors of the metals mobility in the soils was calculated using the equation below:

$$MF = \frac{F1 + F2 + F3}{F1 + F2 + F3 + F4 + F5} \times 100$$

Where F1 = Exchangeable metal content fraction

F2 = Metal content bound to carbonate fractions

F3 = Metal content bound to Fe-Mn oxide fraction

F4 = Metals content bound to organic matter fraction

F5 = Residual metal content fraction

The presence of a high MF value for heavy metals in soil indicates a high level of lability and biological availability (Osakwe, 2010).

6. Data Analysis

All data collected were duplicates of three determinations, statistical analysis were conducted by calculating the mean and standard deviation using statistical software like Microsoft Excel. Results from the data analysis were represented in charts and tables.

III. RESULTS AND DISCUSSION

Table 3.1: Soil pH results with control

Sample Location	Parameter (pH)	
	Distilled water	Distilled water and Calcium chloride salt
Dutsen –Soyaya	4.01	3.52
	3.51	2.94
Mean	3.76	3.23
Control Site	4.79	4.36
	4.64	4.00
Mean	4.72	4.18

Table 3.2: Heavy metals concentrations (Mg/Kg) in sample soils with control

Metals	**Sampling Location / Limits**	**Concentration (mg/kg)**
Co	Dutsen-Souaya A	209.54
	Dutsen-Soyaya B	165.32
	Mean±SD	187.42±31.26
	Control Site Mean	**18.42**
	WHO	**19**
As	Dutsen-Souaya A	309
	Dutsen-Soyaya B	488
	Mean±SD	398.50±126.57
	Control Site Mean	**35**
	WHO	**20**
Cr	Dutsen-Souaya A	71.48
	Dutsen-Soyaya B	42.9
	Mean±SD	57.19±20.20
	Control Site Mean	**36.48**
	WHO	**50**
Ni	Dutsen-Souaya A	27.87
	Dutsen-Soyaya B	16.73
	Mean±SD	22.30±7.87
	Control Site Mean	**3.67**
	WHO	**20**
Mn	Dutsen-Souaya A	125
	Dutsen-Soyaya B	104
	Mean±SD	114.50±14.84
	Control Site Mean	**165.92**
	WHO	**0.04**
Pb	Dutsen-Souaya A	46.1
	Dutsen-Soyaya B	45.3
	Mean±SD	45.7±0.56
	Control Site Mean	**33.29**
	WHO	**10**
Zn	Dutsen-Souaya A	45.7±0.56
	Dutsen-Soyaya B	27.28
	Mean±SD	35.20
	Control Site Mean	**55.5**
	WHO	**250**
Cu	Dutsen-Souaya A	9.19
	Dutsen-Soyaya B	11.29
	Mean±SD	10.24±1.48
	Control Site Mean	**12.40**
	WHO	**2**

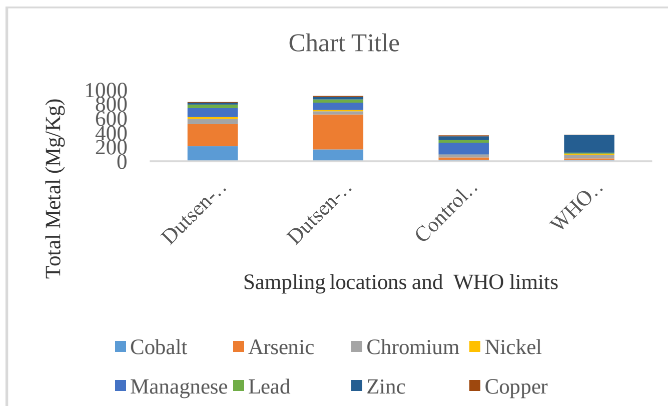

Figure 1: Combined heavy metals concentrations of the shooting range and control point

III.1. Soil pH

The pH results as shown in Table 3.1 showed that the shooting range soil was acidic and more acidic than the control sample values. Sanderson *et al.*, (2012) found that between 7.5 and 46 percent of Pb migrated from surface soils into subsoils in a shooting range with acidic soils (pH 5.4–6.4), compared to only 6–18% in a shooting range with an alkaline pH of 9.3. High heavy metal concentrations, according to a study by Nwaugo *et al.*, (2008), reduce soil nutrient levels, soil moisture, and pH. The effect of pH on the mobilization of Pb in soil was established in a study by Chen *et al.*, (2002) that as more Pb minerals dissolve in acidic pH, the pH will rise. This supports the hypothesis that as concentrated Pb mineral dissolves; the acidification of soil increase. The transformation of metallic Pb to secondary Pb-minerals was faster at 100% Field capacity, in the presence of OM, and at lower pH, according to Ma *et al.*, (2017). While little transformation of Pb occurred in the absence of soil organic matter, and mostly litharge (PbO) were found at higher pH, both hydrocerussite and litharge formed at lower pH. Lower soil pH may increase Ni toxicity in soil-grown plants; further analysis revealed that at lower soil pH, more Ni dissolves, making it more accessible for plant uptake (Dan *et al.*, 2008).

III.2. Heavy Metals Concentration

The mean concentration value of Co (162.50mg/Kg) in the sampled soils were above the Co metal limits as recommended by WHO and the control site as shown on Table 3.2. This suggests increased anthropogenic input of the metals in the shooting range soils via military activities. Co has been found to be used in the manufacture of alloys with Cr, Ni, Al, Cu, Be, and Mo, so this increase could be attributed to military activities on the sites. Which are also used in the automobile industry, as well as the manufacture of military aircraft and ammunition (Royal Society of Chemistry, 2016). Nwaedozie *et al.*, (2013) reported Ni concentration ranging from 5.547 – 22.35mg/Kg in military training areas in Kaduna State, this correlates to similar values recorded in the Dutsen-Soyaya shooting range soils, attributing this high content to the shooting activities, as Ni content in the control site was just 3.67mg/Kg as shown in Table 3.2. However, both values from the sampled soils were within the acceptable limits for Ni in soils.

Cr is a heavy metal that is widely used in a variety of industrial applications. It is primarily used in industrial leather processing and finishing, refractory steel production, drilling muds, electroplating cleaning agents, catalytic manufacturing, and the production of chromic acid and specialty chemicals (Ertani *et al.*, 2017). Mean Cr values in the shooting area soil was 49.32mg/Kg, 36.48mg/Kg for the control site, suggesting high content of the Cr metals in both soils. The mean Cr value in the shooting site was in the same threshold limit with the WHO limit of 50mg/Kg. Because the control site is farmland, the high Cr value could be attributed to pesticides, fertilizers, and manures deposition (Wuana and Okieimen, 2011). According to Osakwe and Okoli (2013), farmlands near busy roads had high NI content as a result of automobile activities. Mn concentrations were alarming in both soils, with the control site's mean Mn value of 165.92 mg/kg being the highest. Both soil samples had values that were above the permissible limits. Sha'Ato *et al.*, (2012) found high levels of Mn in some agricultural farmlands, berating the significant concentrations on soil types and parent rock elemental composition. Ezeofor *et al.*, (2019) also highlighted that the use of agrochemicals, fertilizers, and pesticides in farmlands could also be blamed for high Mn levels. The high Mn in the shooting site was also attributed by Nwaedozie *et al.*, (2013) to metal deposition caused by shooting activities. Pb values were observed in both the shooting sites and control site to be above the WHO permissible limits, suggesting anthropogenic deposition of the metal. In the berm soils of TAB shooting range. Sehube *et al.*, (2017) found elevated Pb concentrations of 38 406.87 mg kg^{-1}. The majority of the shooting range soils had high levels of Pb in the range of 2000mg kg^{-1}, far exceeding the critical value of 400mg kg^{-1} set by the United States Environmental Protection Agency (USEPA). The control site's Zn levels were higher than the shooting site's 33.29 mg/kg, but still within acceptable limits. This increase could be attributed to the use of manures and fertilizers in the control site, which was anthropogenic soil enrichment. Matthee *et al.*, (2016) found that shooters had significantly higher blood lead levels (BLL) than archers, with 36/85 (42.4%) of shooters versus 2/34 (5.9%) of archers having a BLL 10 g/dl (p 0.001).

Natural processes (such as weathering of As-rich minerals in Earth's critical zone and volcanic activity) and anthropogenic activities (such as the use of wood preservatives, mining, and smelting, excessive use of As-based fertilizers and pesticides in agriculture, and irrigation with As-contaminated groundwater) are all examples of As ingression into the environment (Khalid *et al.*, 2017). A significant amount of As was found in the shooting site, with a mean value of 305mg/Kg, indicating high metal deposition due to military activities in the area. As is commonly used in small ammunition for military training operations, according to Bannon *et al.*, (2007), and thus could be present in the shooting site. The As value at the control site was also above the permissible limit, implying that its presence could not be attributed to natural causes. Ifediegwu *et al.*, (2020) found elevated As levels in agricultural soils, plant shoots, and roots, criticizing contaminants in pesticides, herbicides, and fertilizers for the rise. Cu was also found to be above permissible limits in both sampled soils, with mean values of 7.74 g/kg for shooting range soil and 12.40 mg/kg for control site soil. According to Robinson *et al.*, (2008), the geometric mean concentrations of Pb, Sb, Cu, and Ni deposited in Swiss rhizospheric soils by military activities were 10,171 mg/kg, 5067 mg/kg, 4125 mg/kg, and 917 mg/kg, respectively. In Small-arms firing ranges, Rodrguez-Seijo *et al.*,(2016) recorded concentrations of Pb, Zn, Cu, Cr, and Ni ranging from 55 to 6309, 34 to 264, 19 to 98, 40 to 79, and 11 to 33 mg kg1, respectively. In some agricultural topsoils in Kogi, North Central, Nigeria, Emurotu and Onianwa, (2017) found Cd levels ranging from 0.07 to 9.80 mg/kg, Co 0.05–38.1 mg/kg, Cu 0.33–16.9 mg/kg, Ni 3.81–93.1 mg/kg, Pb 4.45–47.7 mg/kg, and Zn 5.02–81.4 mg/kg, indicating anthropogenic input for the high levels of the metals.

III.3. Speciation and Mobility Factor of the heavy metals

The following is the Co distribution in the shooting range soil: Residual > Organic > Fe – Mn Oxide > Bound to carbonate > Exchangeable fractions as shown in Figure 2 and 3. The bioavailable fraction had a concentration of 45.33% of the metal, while the non-bioavailable fraction had a concentration of 54.67%. Despite the large amount of Co in the non-bioavailable fraction, the metals had a high mobility factor of

44.50%, implying that further weathering and increased metal deposition could eventually lead to soil toxicity in shooting sites. In the control site, large concentrate of the metals was located in the non-bioavailable fractions as shown in Figure 5 with a mobility factor of 23.30 as shown in Figure 6. In their study, Lange *et al.,* (2014) found that variations in copper accumulation in plant shoots were primarily influenced by Cu adsorbed by the Mn and Fe oxides fractions, whereas variations in Co accumulation were primarily influenced by Co free and Co adsorbed by the organic matter and Fe-Mn fractions.

According to the distribution of As in the shooting soil, the fraction Fe – Mn Oxide > Residue > Organic > Bound to carbonate > Exchangeable was the least occupied. In the bioavailable fraction, 55.94% of the As metal was readily available. The mobility of the metals was found to be 55.93%, indicating that the plants are highly susceptible to As absorption in the shooting range soil. As in the control site had a low MF of 19.10% with the non-bioavailable fractions being predominant with F4 with the highest metal concentration. As has high mobility and phytoavailability in acidic soil conditions (<pH 5.5). This is due to As being converted into a more soluble As fraction (AsIII) at low soil pH (Signes-Pastor *et al.,* 2007). According to Itabashi *et al.,* (2019), there is a poor correlation in As concentrations between water extraction and total digestion (r = 0.38), implying that the total concentration is not a reliable index for assessing the potential environmental risk of As.

Exchangeable > Fe – Mn Oxide > Bound to carbonate > Organic > Residual fractions are the Cr speciation order. The bioavailable fractions contained 89.42% of the total Cr concentration in the soil, with the exchangeable fraction having the highest Cr active site. Despite almost exceeding the WHO total content Cr limits of 50 mg/kg, it is clear that 11% of the metals are inactive, according to the speciation results. The presence of Cr for plant adsorption and animal consumption was demonstrated by a high Cr uptake mobility factor of 79.43%. The non-bioavailable fraction were predominant with the highest concentration of Cr with a high MF of 33.40%, enhancing increased availability of plant absorption of the metal. At pH <4, Cr(III) is naturally present in insoluble inorganic compounds; as the pH rises, Cr(III) is more commonly found in hydrolyzed forms, which are already not very soluble and tend to bind organic substances. On the contrary, Cr(VI) is highly mobile due to the formation of soluble inorganic compounds such as chromates, which are both bioavailable and toxic (Adriano,1984; Salmani and Fazaelipoor, 2016). Because of the significant presence of Cr in the soluble and exchangeable fraction, Bartlett (1997) demonstrated that in soils with high Cr concentrations, both the mobility and bioavailability of this metal increase. Furthermore, if the pH is right and MnO2 is present, Cr(III) can be oxidized to the toxic hexavalent form, even if this is a rare occurrence.

Nickel can be found in soils in a variety of forms, including adsorbed or complexed on organic cation surfaces or inorganic cation exchange surfaces, inorganic crystalline minerals or precipitates, and water soluble, free-ion or chelated metal complexes (Iyaka, 2011). High concentration of Ni on the shooting sites were observed to be present in the non-bioavailable fraction at a value of 40.31% as depicted in this speciation order: Fe – Mn Oxide > Exchangeable > Bound to carbonate > Residual > Organic. Despite having 59.69% of its metal content in the bioavailable (soluble) fractions, a high mobility factor of 59.71% showed increased uptake tendency of the metals to for adsorption and more during environmental degradation such as weathering. Similar speciation results was also recorded on the control soil with the concentrate of the Ni metals in the Non-Bioavailable fractions. Previous studies have shown that Ni is mostly found co-precipitated as Fe–Mn oxides, and its sorption in this form is particularly pH dependent, most likely because the surface charge on the sorbent is affected by pH. (Bodek *et al.,* 1988).

Mn concentrations in the soils of the shooting sites were mostly in the bioavailable fraction, with F2 and F3 accounting for a large percentage of the metal presence in that fraction (18.33 and 39.28% respectively). The following is a list of Mn speciation in soils: Residual > Fe – Mn Oxide > Bound to carbonate > Organic > Exchangeable. Nwaedozie *et al.,* (2020) also recorded Manganese speciation in Kwanyar Doya shooting site as follows: Residual > Fe – Mn Oxide > Bound to carbonate > Organic > Exchangeable. The total metal content in the soil indicated that it was a contaminant, with values exceeding the allowable limits. The high mobility factor of 69.39% makes Mn readily available for plant absorption and animal consumption. Furthermore, this could lead to for plant poisoning via Mn uptake. Although high MF values show a typical norm of increased Mn movement for plant consumption, Mn speciation values on the control site revealed that more of the metal was found to be predominate in the non-bioavailable fraction. Mn oxides are also important in the oxidation of Cr(III) to Cr(IV) in soils, and the amount of Cr(VI) produced by oxidation of Cr(III) by Mn oxides is related to the types of Mn oxides in nodules, such as birnessite, lithiophorite, todorokite, lithiophorite, and lithiophorite (Tan *et al.,*2005). According to Schulte and Kelling (1999), manganese levels in acidic sandy soils are likely to be high. Excess manganese levels are more common in acidic soils (pH), particularly when these soils are depleted in organic matter and temporarily flooded.

Pb concentrations in the shooting soils were dominant in the non-bioavailable fractions with the speciation results as follows: Residual > Organic > Fe – Mn Oxide > Exchangeable > Bound to carbonate. Pb total metal content in the soil were higher than the permissible limits with its mobility factor in the soil at 34.98%. Despite its high MF, Pb total metal content poses no environmental threat. The speciation results for the control site also revealed that the metal concentrations were mostly present in the non-bioavailable fractions, with F4 having the largest deposit of pb metal. Kelebemang *et al.*, (2017) reported that Pb mobility in berm soils was found to be over 90% in all seven shooting ranges in Eastern and North-Eastern Botswana, indicating high Pb liability. The bioavailability index of Pb was reported to be within the range of 60–90%, indicating that the majority of the Pb can be absorbed by plants. Reigosa-Alonso *et al.*, (2014) recorded Pb total content to be high at both soil depths (0–15 and 15–30 cm) at shooting ranges, but Cu, Ni, and Zn had lower significance levels. Copper, Ni, and Zn are the most common metals found in the residual fraction (95% of total content in all cases). Pb, on the other hand, was found to be highly associated with exchangeable fractions (21–52%), indicating that it has a high mobility at both depths. The studied soils have acidic values and low levels of Al, Fe, and Mn oxides, which favours Pb migration through the soil profile and potential transformation to more mobile forms (Pb^0 to Pb^{2+} and Pb^{4+}).

Zn is an important component in the development of soil and plants, despite being used in the manufacture of military artillery. Free zinc (Zn^{2+}) is one of the most soluble and mobile divalent trace metal cations in acidic conditions (McBride, 1994).The concentration of Zn in the shooting soil was within permissible limits, with speciation results of Zn occurring in the bioavailable region: Fe – Mn Oxide > Bound to carbonate > Residual > Organic > Exchangeable. Despite its high mobility factor of 89.67%, its low concentration in the soil poses no environmental risk**.** The control site also had a high MF value of 47.58%, with most of the Zn metals occupying the non-bioavailable fractions. Nwaedozie *et al.*, (2020) found the following zn speciation in Kawnar-Doya shooting soils: Fe – Mn Oxide > Residual > Organic > Bound to carbonate > Exchangeable fractions, indicating that Zn was more widely distributed in non-reactive than reactive fractions.

Cu was primarily found in the non-bioavailable fractions, with the following speciation results: Residual > Carbonate bound > Fe – Mn Oxide > Exchangeable > Organic. Cu has a mobility factor of 56.82%, making it easily accessible to plants for absorption and weathering effects on the environment. Similar MF value of 58.04% were recorded in the control site, with the bioavailable fraction being the most occupied. Liu *et al.*, (2014) also used Tessier's sequential extraction method to investigate the concurrent speciation of Pb and Cu in soil, and discovered that the chemical speciation distribution order is as follows: FeMnO-Pb > Org-Pb > Carb-Pb > Exch-Pb > Resid-Pb. Cu distribution characteristics can also be listed in the following order: Carb-Cu > Exch-Cu > Resid-Cu > Org-Cu > FeMnO-Cu > Carb-Cu > Exch-Cu. It can be seen that heavy metal Pb poses a much greater risk of environmental contamination.

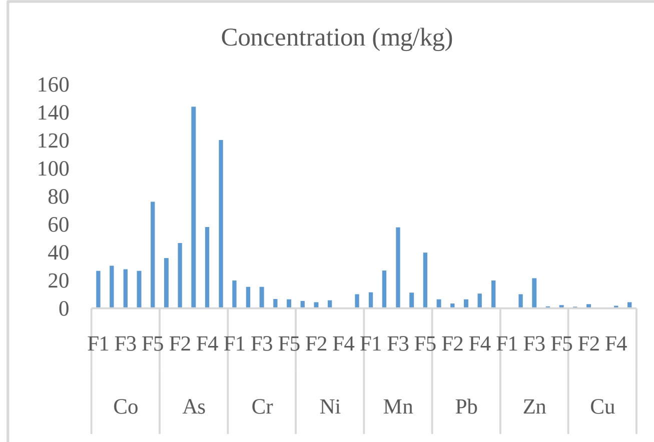

Figure 2: Mean Distribution values of the various heavy metals in Dutsen-Soyaya Shooting range soils.

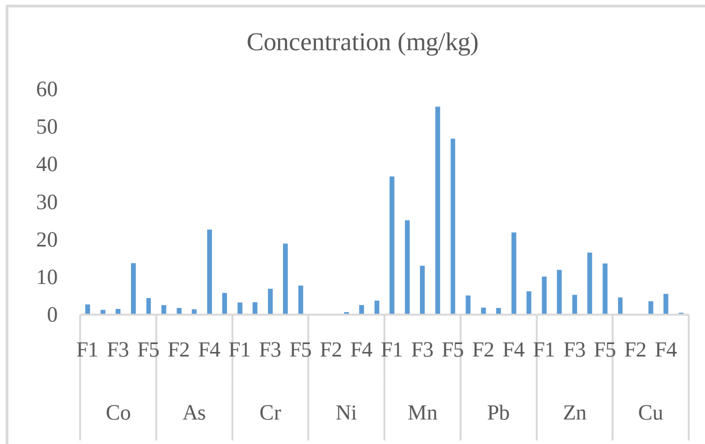

Figure 3: Mean Distribution values of the various heavy metals in the Control site.

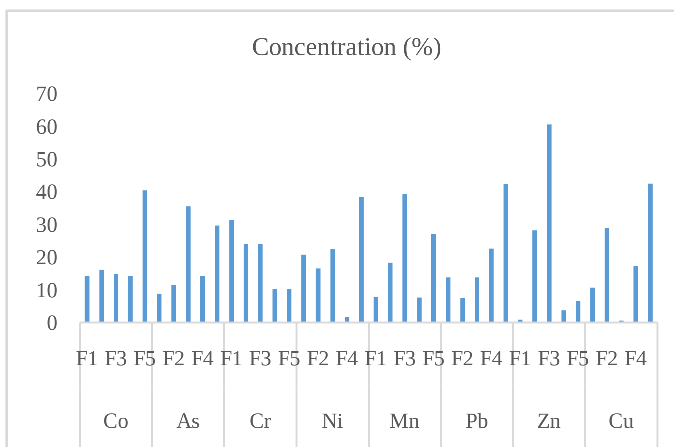

Figure 4: Percentage Distribution of the heavy metals in the shooting range soils.

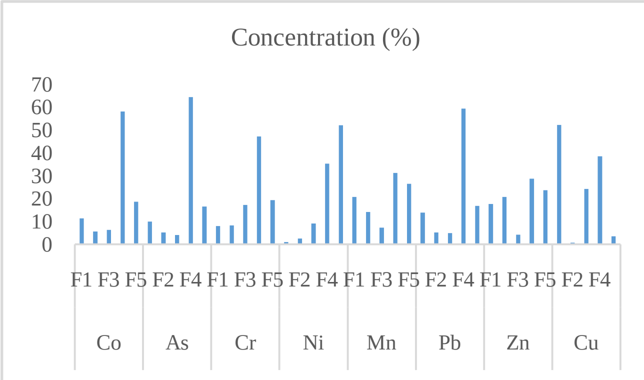

Figure 5: Percentage Distribution of the heavy metals in the Control site soil.

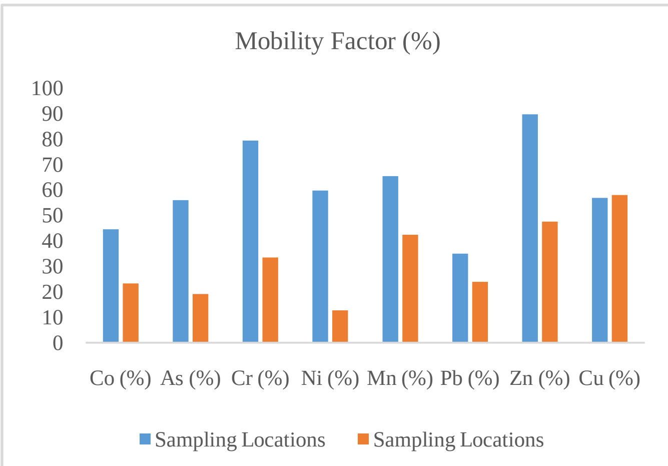

Figure 6: Mobility Factor of the various heavy metals in the sampled soils.

IV. CONCLUSION

The Dutsen-Soyaya shooting range is operated by the Nigerian Defence Academy and is an important part of the training of military cadets and professionals in warfare and artillery use. According to this study, the shooting site was found to be highly contaminated with heavy metals, which are a major component of the weapons used on site. The results of the speciation and mobility factors show that migration increases as soil acidity rises, with the majority of these metals concentrating in the bio-available fractions. On the other hand, this would result in plants rapidly absorbing metals, which would then be consumed by animals. To ensure the future use of this military heritage is preserved for future use, phyto-remediation of affected soil should be implemented, as it will help to reduce toxic metal deposits in the soil while also preserving the environment and the site.

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