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Evaluation of Some Heavy Metals (Pb, Zn, Cu and Sb) in Soil and Plants collected in Air Force Heavy Metals Military Shooting Range in Kaduna, Nigeria

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Abstract **– The accumulation of heavy metals of Pb, Zn, Cu, and Sb in soil and plant samples in Air Force shooting range were evaluated using Atomic Absorption Spectroscopy and values obtained were compared with WHO standards. The values of Cu (41.04±0.11, Zn 41±0.14, Sb (9.12±0.11 mg/kg) were within limits of WHO while that of Pb (495.75±0.10 mg/kg) was above WHO standards limits of soils. The results showed that the total metal concentrations of heavy metals in the soils' sample have the sequence Pb>Zn>Cu>Sb while in plant samples the trend is Pb>Sb>Zn>Zn>Cu. *S. acuta* accumulated Pb and Cu more in the leaves (120.66±0.15 and 125.36±0.12 mg/kg) respectively while *U.lobata* accumulated Pb and Cu more in the leaves (120.87±0.12 and 125.37±0.12 mg/kg) respectively than in the roots. The plants (*S. acuta, Amorphophyllus sp,*and *U. lobata*) have translocation factor (TF) greater than one (>1) for Zn and Sb. This indicates that the soil in the shooting range is contaminated with Pb and all the plants studied have the phytoremediation potential for Sb and Zn in soil.**

Keywords **– Heavy Metals, Shooting Range, Native Plants, Bioaccumulation Factor, Translocation Factor.**

I. Introduction

Heavy metals make a significant contribution to environment as a result of human activities such as mining, smelting, electroplating, intensive agriculture, sludge dumping and melting operations (Welch, 1995). All heavy metals at high concentration have strong toxic effects and are regarded as environmental pollutants (Page *et al*., 1982).

To defend Nigerian national interest, the Armed Forces require shooting ranges to train and maintain the capabilities of soldiers in marksmanship. It has been recognized that this practice can result in significant contamination of soil with spent bullets. Lead, copper, zinc and antimony are primary chemicals used in the production of these bullets. Pb is toxic to humans having deleterious effects on organs system particularly the central nervous system, the kidney and blood (Tong *et al*., 2000). It is readily accumulated by plant roots (Sanderson *et al*., 2010). Cu is toxic at low concentration and is known to cause brain damage in mammals (DWAF, 1996). Zn is toxic to plants (Broadley *et al*., 2007) while its excessive absorption by humans suppresses Cu and Fe absorption. McCallum (2005) reported that process workers in Sb industry suffered mostly from skin irritations (Sb spots) and upper respiratory tract irritations.

Contamination of shooting ranges has been under increased scrutiny in recent years due to weathering of spent bullets. Spent ammunition is subject to weathering when it comes into contact with the soil or water. Metals may be oxidized to a number of secondary forms such as oxides and carbonates which are soluble and serve as a source that can release labile metals into the soil. Peddicord and LaKind, (2000) have identified in addition to Pb, Cu (casing of the bullet), Ni and Zn (alloys with copper), Sb (a hardening agent) as contaminant of concern at shooting ranges. Robinson *et al*., (2008) examined the plants uptake of trace element on Swiss military shooting range and found that over 400 tons of Pb enters the soils annually at some 7000 military shooting ranges scattered throughout the country. Zellmer and Schneider (1993) measured some metal concentrations in leaves from assorted species on shooting ranges from Grafenwohr, Germany. They found that the concentrations of most metals fell within the normal range for plants (Baker and Chesnin, 1975).

In Nigeria there are several shooting ranges and the concentrations of heavy metals in the soils and plants have not been assessed. This necessitated this investigation. For this reason the concentrations of Pb, Zn, Cu and Sb were examined in soil and native plants growing in shooting range of Nigeria Air Force, Kaduna.

II. Materials and Methods

2.1 Sampling

The plant and soil samples used in this study were collected from the Air Force shooting range located in Kaduna, Northern Western Nigeria. The entire area was divided into 5 sections.

For plant sampling, four different plants namely *S. acuta, Amorphophyllus Sp, C.dactylon and U.lobata* were used. Three samples of each plant species were collected at different points in a given section. Each plant sample was uprooted to include the roots and soil samples were also collected from the point of sampling. The sampled plants were sorted according to species, collection points and labeled accordingly.

For soil sampling, 10g of the soil samples at root zone were collected at a depth of 0- 15cm^3 using soil auger at 10 different points within a section and harmonized to form a composite sample (Carter and Gregorich, 2006).

2.2 Soil Analysis

The soil samples (10g) were oven dried at 100^{0}C for 1 hour, then ground into fine powder and sieved through 250µg mesh. Total metal contents were extracted by acid digestion (Ramos *et al.*, 1994). The sample (1.0g) was digested with a mixture of 4.0 cm^3 of 70% perchloric acid and concentrated nitric acid (2.0 cm^3) and heated for 12 hours at 100^0C in an oven. A resulting white ash was dissolved in 2.0 cm^3 of 1.0M HCl. The digest was filtered into a 50 cm^3 standard volumetric flask. The mixture was made up to the mark with double distilled water. Total concentrations of metals (Pb, Zn, Cu and Sb) in the prepared samples were determined using Atomic Absorption Spectrophotometer (Shimadzu AA-700F/G).

2.3 Plant Analysis

The plant samples were first separated into roots, stems and leaves, then washed with distilled water and oven dried at 70^0C for 2 hours (Larry and Morgan, 1986). They were ground into fine powder sieved and stored in a labeled bottled until analysis. 0.5g of prepared plant samples were digested with $5.0cm^3$ of concentrated HNO_3 and $5.0cm^3$ of 70% $HClO_3$ and placed on a hot plate for 5 minutes after which $20cm^3$ of deionised water was added. On cooling, the digest was filtered into $100.0cm^3$ volumetric flask. The mixture was made up to mark with deionised water (Horwitz, 1980). Total concentrations of Pb, Zn, Cu and Sb in the prepared samples were determined by Shimadzu AA-700F/G model Atomic Absorption Spectrophotometer (AAS).

III. Results and Discussions

Table 3.1 shows the mean total metal concentrations in soil in Air Force shooting range in Kaduna State, Nigeria.

Table 3.1: The concentration of heavy metals in the soil (mg/kg) collected at different plots of Air Force Shooting Range, Kaduna.

Plots	Metal Concentration (mg/kg)			
	Pb	Cu	Zn	Sb
1	11.97	12.445	36.74	9.80
2	843.85	76.55	60.16	4.15
3	398.35	30.925	27.625	8.10
4	323.425	25.935	43.915	14.32
5	801.135	59.35	41.400	9.23
Average	495.745	41.041	41.968	9.117
WHO	100	100	300	<10*

Key: WHO (1960), Source: *Filella *et al.*, (2002)

The result revealed that the mean values of 495.75 mg/kg, 41.04 mg/kg, 41.97 mg/kg and 9.12 mg/kg of Pb, Cu, Zn and Sb respectively. Of all the heavy metals examined in the soil from the studied area, the mean concentration of Sb (9.12 mg/kg) was the lowest followed by Cu (41.04 mg/kg), Zn (41.97 mg/kg) and Pb (495.75 mg/kg). The values of Cu (41.04±0.11 mg/kg), Zn (41±0.14 mg/kg), Sb (9.12±0.11 mg/kg) were within limits of WHO while that of Pb (495.75±0.10 mg/kg) was above WHO standards limits of soils. The concentration of Pb is almost 4 times higher than WHO standards which show that the activities in the study area may be responsible for the high concentration. The high concentration of Pb is not unexpected as the activities in this area involve bullet disintegration of which Pb is a component (Rooney *et al.*, 1999).

Table 3.2: Heavy Metal Concentrations (mg/kg) in Plant Parts Collected at the Shooting Range of Air Force, Kaduna.

Plant Species	Pb	Cu	Zn	Sb
SA root	52.43±0.10	ND	40.68±0.11	137.79±0.05
SA stem	68.63±0.12	ND	85.95±0.12	161.11±0.06
SA leaf	120.66±0.15	125.36±0.12	58.10±0.13	104.44±0.01
AS root	117.58±0.13	5.59±0.13	40.08±0.11	16.78±0.01
AS stem	182.15±0.11	1.92±0.11	39.07±0.12	13.89±0.01
AS leaf	47.23±0.12	8.65±0.12	24.62±0.10	13.93±0.01
UL root	52.57±0.14	ND	40.62±0.14	137.84±0.01
UL stem	68.65±0.11	ND	85.97±0.13	161.11±0.01
UL leaf	120.870±0.12	125.37±0.12	58.136±0.12	104.46±0.10
CD root	118.63±0.10	3.73±0.13	81.61±0.11	31.90±0.11
CD stem	98.06±0.11	7.69±0.14	58.13±0.12	25.34±0.19
CD leaf	136.75±0.13	3.59±0.11	9.70±0.13	22.22±0.12
HA root	500.31±0.13	34.53±0.12	43.83±0.13	30.02±0.12
HA stem	355.15±0.13	70.03±0.11	65.81±0.14	12.05±0.12
HA leaf	145.16±0.10	ND	58.51±0.10	16.20±0.10

Key: SA = *S.acuta*, AS= *Amorphophylus sp*, UL= *U. lobata*, CD= *C.dactylon*, HA= *H. annus*

The Cu (41.041 mg/kg) concentration is within limits of WHO permissible limits in soil. Cu is a component of bullet, Craig *et al.*, (2002) reports evidence of Cu fragments associated with short-range, low angle shotgun shots at a shooting range in Virginia. Borkert *et al.*, (1998) reported that Cu level exceeding 20 mg/kg in shoots or leaves will cause toxic effects. The concentration of Zn 41.968 mg/kg in within WHO permissible limits. Yoon *et al.*, (2006) reported that soil in northwest Jacksonville, Florida was contaminated with high concentration of Pb (20-990 mg/kg), Cu (20-990 mg/kg) and Zn (195-22000 mg/kg). They said that all the three metals are likely from similar sources of contamination. This agrees with our findings where Pb, Cu and Zn are contaminants of concern in the Air Force shooting range introduced from disintegration of bullets. The concentration of Sb (9.117 mg/kg) is lower than WHO permissible limits in soils. Sanderson *et al*., (2010) reported Sb (600 mg/kg) in shooting range soil in Australia.

The Table 3.2 showed that *S.acuta* accumulated Pb and Cu more in the leaves than in the root while only Sb and Zn were more in the stem than in the leaf and root. This means that the accumulated metals are not stored in the root but are fairly distributed to all parts of the plant. The same pattern was observed in the case of *U.lobata*. However, *C.dactylon*, showed its deviation in Cu, Zn and Sb accumulation with more metals in the root than in stems and leaves. This may be that the metals are stored more in the root and lesser in other parts. This situation is the same for absorbed Sb by *C.dactylon* and *H.annus* respectively. The general pattern observed in this work (shoots accumulate more metals than roots) is in conformity with the work of Faruruwa *e al*., (2013).

The results of BAF and TF for all the heavy metals are reported in Table 3.3 below:

Table 3.3: Bio accumulation and Translocation Factor of SA, AS, UL and CD for Pb, Cu, Zn and Sb

Plant Species	Pb	Cu	Zn	Sb
S. acuta	0.382[a]	3.055[a]	3.434[a]	29.127[a]
	3.610[b]	0.00[b]	3.51[b]	1.927[b]
Amorphophyllus Sp	0.463[a]	0.257[a]	1.518[a]	3.051[a]
	1.951[b]	1.891[b]	1.5891[b]	1.657[b]
U.lobata	0.382[a]	3.055[a]	3.433[a]	29.130[a]
	3.605[b]	0.00[b]	3.548[b]	1.930[b]
C.dactylon	0.473[a]	0.275[a]	1.516[a]	5.217[a]
	1.978[b]	3.025[b]	0.828[b]	1.491[b]
H.annus (Control)	1.678[a]	2.61[a]	5.90[a]	1.47[a]
	0.23[b]	2.03[b]	2.84[b]	0.944[b]

Key: a = Bioaccumulation factor, b = Translocation factor, BAF=Bioaccumulation factor,TF = Translocation factor

The results of BAF and TF are in Table 3.3. The BAF value was expressed by the ratio of $C_{shoo}t/C_{soil}$ (Robinson *et al., 2000,* Ma *et al.*, 2001) where C_{shoot} and C_{soil} are metals concentration in the plant shoot (mg/kg) and soil (mg/kg) respectively. The BAF represents the contaminant concentration in plants comparing with the environment concentration (Scragg, 2005). The BAF highest for Pb was 0.473 of *C.dactylon* and lowest 0.382 of *S.acuta*. The control result gives BAF greater than one (>1) for all metals. The BAF factors were varied as many plants had BAF greater than one while few had BAF lower than one (Table 3.3).

The translocation factor (TF) values for heavy metals are presented on Table 3.3. The TF value for metals within the plants was calculated as the concentration of metal in the above ground part of the plant (shoot) divided by the concentration in the root (Baker and Brooks, 1989, Zhang *et al*., 2002).

The TF highest for Pb was 3.61 in *S.acuta* and lowest for *Amorphophyllus sp* with value of (1.951). The TF values were greater than one (>1) for Pb in SA, AS and CD; SA, AS, UL and CD for Sb; AS, CD for Cu; SA, AS and UL for Zn. The control result (*H.annus*) gives TF<1 for all metals except for Zn (2.84) and Cu (2.03).

A plant's ability to translocate metals from the roots to the shoots is measured using the TF. TF greater than one (>1) represent that translocation of metals effectively was made to the shoot from the root (Baker and Brooks, 1989, Zhang *et al*., 2002) This is most likely due to efficient metal transporter system and probably sequestration of metals in leaf vacuoles and apoplast (Lasat *et al*., 2000). TF >1 were determined in metal accumulators whereas TF lower than one (1<) in metal excluder species. The data presented indicate metal (Pb, Sb, Cu and Zn) accumulated by the plants species were largely transported to the shoots from roots as shown by general TF values which is greater than one (>1, Table 3.3). Exceptions occurred in *S.acuta* for Cu (TF = 0) and CD for Zn (TF = 0.83).

All the four plants samples studied have both BAF and TF greater than one for Sb and Zn. Therefore these plants can be used to remove these metals from the environment.

IV. Conclusion

Based on the results obtained in this study, it can be concluded that:

- Air Force shooting range is contaminated with Sb, Zn, Cu and Sb
- All the plants studied (*S. acuta*, *Amorphophyllus sp, U. lobata and C. dactylon*) can be a suitable bioremediator for Zn and Sb.

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