Concentration of heavy metals in the soil and translocation with phytoremediation potential by plant species in military shooting range

Y. Magaji\textsuperscript{1*}, G. A. Ajibade\textsuperscript{1}, V. M. Y. Yilwa\textsuperscript{1}, J. Appah\textsuperscript{1}, A. A. Haroun\textsuperscript{1}, I. Alhaji\textsuperscript{1}, M. M. Namadi\textsuperscript{2}, A. I. Sodimu\textsuperscript{3}

\textsuperscript{1}Department of Biological Sciences, Nigerian Defence Academy, P.M.B. 2109 Kaduna, Nigeria
\textsuperscript{2}Department of Chemistry, Nigerian Defence Academy, P.M.B. 2109 Kaduna, Nigeria
\textsuperscript{3}Department of Forestry Technology, Federal College of Forestry Mechanization, P.M.B. 2273 Afaka Kaduna, Nigeria

*E-mail address: magajiyakubu01@gmail.com

ABSTRACT

Concentration of seven (7) metals (Pb, Cu, Zn, Mu, Ni, Cr, and Cd) in the samples of soil and some plant species collected from Kachia military shooting range were determined. The mineral ions were assayed using the acid digestion method and atomic absorption spectrophotometry (AAS). Physicochemical parameters (pH, EC, Bulk density, water holding capacity and Total Nitrogen) of the soil samples were also determined. Of the 7 metals determined in the soils samples, the concentration of Pb ($14.85 \pm 6.78$ mg/kg\textsuperscript{-1}) was the highest compared to the concentrations of other metals. Physicochemical parameters were within the range that allows effective phytoremediation. Cu showed the lowest concentration ($0.55 \pm 1.68$ mg/kg\textsuperscript{-1}). Ni was below the detectable limit in most of the samples. Similarly, concentrations of Pb ($12.30$ mg/kg\textsuperscript{-1}) in the shoot of \textit{Albizia zygia} among other metals were higher than those of the other metals in the plant tissues. Concentration of Cd ($0.07$ mg/kg\textsuperscript{-1}) in the root of \textit{Eragotis tremula} was the lowest. Generally, metal ion concentration in the soil and plant samples of the shooting range (polluted site) significantly differed from those of the non-polluted site (P<0.05). \textit{Combretum hispidium} among the plant species had the highest translocation factor ($T_F = 2.91$). Although the $T_F$ was higher in the plant of the polluted site $T_F >1$, reasonable amount of them were retained within the underground tissues (roots).

Keywords: Heavy metals, Translocation, Phytoremediation, Physicochemical parameters
1. INTRODUCTION

Heavy metals are released to the environment usually through anthropogenic activities such as firing of ammunitions, mining, electroplating, smelting etc. (Samarghandi. et al, 2007). They constitute a major pollutant and make a significant impact to the environment.

According to Page et al (1982), all heavy metals have strong toxic effect, hence they can contaminate the environment. In contemporary times the possibility of using certain species of plants to decontaminate environments polluted by the accumulation of heavy metals, a process referred to as phytoremediation, has been seen to be very promising and reliable (Gurbisu and Alkorta, 2003).

In the process of phytoremediation, plant roots play a very vital role in the cleanup of the metals as they are usually located in the soil. Phytoremediation by plants can be achieved through filtration, adsorption, cation exchange and plants induced chemical changes in the rhizosphere (Dumbabin and Bowmer, 1992). It has also been reported that plants, notably *Thalaspi caerulescens*, *Arabidopsis thaliana*, *Phragmites australis* can be used in the cleaning up of environments polluted by heavy metals (Cunningham and OW, 1996; Delhaize, 1996 and Ye et al., 2001)

Generally, factors such as stage of plant growth, variations in plant species and characteristics of the metals affect their absorption rates and accumulation. (Nouri et al, 2009). Guilizzoni (1991) also reported that physiological adaptations control metals accumulations by a process of sequestering metals into the roots. Consequently removal of metals by plants can be greatly enhanced by the selection of plant species.

The knowledge about the potentials of different plants to absorb, accumulate and translocate metals under varying condition is necessary with regard to the choice of plants for effective and efficient phytoremediation process on polluted environment. Therefore, the concentrations of metals such as Pb, Cu, Zn, Mn, Cr, Ni, and Cd were determined in the samples of soil and 8 wild plant species, 2 from each floral groups, that is trees, shrubs, herbs and grasses, found growing within the study area and a neutral area not subjected to the impact of shooting range site (Ama et al, 2017; Chukwuemeka, 2017; Sunday, 2017).

2. MATERIALS AND METHODS

Study area

The research was conducted at the site of shooting range which is at 5km East of Kachia, Kaduna State. Established in 1965, the area covered 24.94 sq km, centered by longitudes 9°55’N and 7°58’E at an elevation of 732 m above sea level (Fig. 1). The general profile of the area showed a topography that is undulating and a vegetation that is typical of the guinea savannah. The soil types in the area vary from point to point and it includes: sandy, sandy-loam, clay, and clayed loam etc. It is a common ground for the training of military officers, cadets and soldiers from different military formations.
Fig. 1. Map of Kaduna State Showing study area (Nigerian Army Shooting Range)
Source: Geography Department NDA Kaduna
Soil Sampling and Analysis

Soil samples were taken from one of the objectives (impact sites) in both wet and dry seasons within the study area at the distances of 200 m and 400 m from the starting point using soil auger which was deepened into the soil to the depth of 15 cm. After air drying for 2-3 weeks 10g of each soil samples were taken into a clean dried beaker and oven dried at 100°C for 1hr. The dried soils were pounded and sieved through 250 μg mesh size. Samples were then analysed for total metals (Pb, Cu, Zn, Mn, Ni, Cr, and Cd) pH, electrical conductivity (EC), bulk density and water holding capacity after pretreatments due for each test. Total metal concentrations were extracted by triacid digestion method (Alloway, et al 1990). The pH and EC were measured using pH meter and EC meter respectively (Rhoades, 1982). Bulk density and water holding capacity and total nitrogen were determined as reported by Anderson and Ingram (1989).

Plant Sampling and Analysis

Eight plant species, two of each of the 4 plant groups (trees, shrubs, herbs and grasses) were collected from the four locations within the study site from February to July, 2010. They were transferred to the laboratory of the department of Biological Sciences, NDA. They were identified in the herbarium and preserved for three (3) weeks. The species found consisted of 8 genera and 7 families (Table 1) out of which 2 species belonged to Fabaceae, forming the most abundant species in the metal polluted site. Samples of the plants were thoroughly washed using running tap water and rinsed with deionized water. Shoots and roots of the plants were separated and oven dried at 70 °C to constant weight (Larry and Morgan, 1989). Oven dried samples were then weighed and ground into powdery form for chemical analysis. Concentrations of metals (Pb, Cu, Zn, Ni, Cr and Cd) of the plant samples were determined after triacid digestion using atomic absorption spectrophotometer (AAS) (GBC Avauta, Australia (Nouri, 2009).

Table 1. Selected Plant Species Studied for Mineral ion Speciation and Their Families

<table>
<thead>
<tr>
<th>Plant Species</th>
<th>Family</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albizia zygia</td>
<td>Fabaceae</td>
</tr>
<tr>
<td>Vitellaria paradoxa</td>
<td>Mimosoideae</td>
</tr>
<tr>
<td>Isobelina doka</td>
<td>Fabaceae</td>
</tr>
<tr>
<td>Combretum hispidium</td>
<td>Combretaceae</td>
</tr>
<tr>
<td>Laggera aurita</td>
<td>Asteraceae</td>
</tr>
<tr>
<td>Urena lobata</td>
<td>Malvaceae</td>
</tr>
<tr>
<td>Andropogon gayyanus</td>
<td>Poaceae</td>
</tr>
</tbody>
</table>
3. DETEMINATION OF TRANSLOCATION FACTOR

Translocation factors (TF) is the ability of plant to accumulate, tolerate and translocate metals from underground tissues to shoot. It was determined for each plant by calculating the ratio of metal concentration in shoot to the concentration in the root using the formula below for each plant (Nouri, 2009; Baker and Brooks, 1989; Zheng et al., 2002; Fayiga and Ma, 2006)

\[ TF = \frac{[Metal]_{shoot}}{[Metal]_{root}} \]

4. RESULTS

Accumulation of Metals in 4 Locations of the Study Site.

As shown in Fig. 2, content of the heavy metals in the soil were high but varied greatly (Table 2). Out of the 7 metals detected, average concentration of Pb (14.85 ± 6.79 mg/kg) was the highest and the lowest concentration was observed in Cu (0.55 ± 1.66 mg/kg). Soils in the study site were alkaline with an average pH of 7.2 which were suitable for plant growth and phytoremediation. The average EC of the soil was 8.11 µ/cm. total nitrogen and average moisture content and total N were approximately 0.5% and 25% respectively.

Table 2. Chemical and physicochemical characteristics of soils of the study area (means ± SE)

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Concentrations (mg/kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PS</td>
</tr>
<tr>
<td>Pb</td>
<td>14.85 ± 6.78</td>
</tr>
<tr>
<td>Cu</td>
<td>0.55 ± 1.68</td>
</tr>
<tr>
<td>Zn</td>
<td>1.04 ± 0.32</td>
</tr>
<tr>
<td>Mn</td>
<td>8.64 ± 1.28</td>
</tr>
<tr>
<td>Ni</td>
<td>BDL</td>
</tr>
<tr>
<td>Cr</td>
<td>14.55 ± 1.45</td>
</tr>
<tr>
<td>Cd</td>
<td>1.84 ± 0.27</td>
</tr>
<tr>
<td><strong>Physicochemical Parameters</strong></td>
<td></td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>7.21</td>
</tr>
<tr>
<td><strong>EC (µ/cm)</strong></td>
<td>8.11</td>
</tr>
</tbody>
</table>
Table 3. Translocation factors ($TF = \frac{[Metal]_{shoot}}{[Metal]_{root}}$) in plant species

<table>
<thead>
<tr>
<th>Species No</th>
<th>Species</th>
<th>$Pb$</th>
<th>$Cu$</th>
<th>$Zn$</th>
<th>$Mn$</th>
<th>$Ni$</th>
<th>$Cr$</th>
<th>$Cd$</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>$A$ zygia</td>
<td>1.41</td>
<td>BDL</td>
<td>1.49</td>
<td>1.69</td>
<td>BDL</td>
<td>1.13</td>
<td>0.06</td>
</tr>
<tr>
<td>02</td>
<td>$V$ paradoxa</td>
<td>1.22</td>
<td>BDL</td>
<td>1.21</td>
<td>1.31</td>
<td>BDL</td>
<td>1.17</td>
<td>0.51</td>
</tr>
<tr>
<td>03</td>
<td>$I$ doka</td>
<td>1.01</td>
<td>1.01</td>
<td>0.96</td>
<td>1.20</td>
<td>0.03</td>
<td>1.10</td>
<td>2.03</td>
</tr>
<tr>
<td>04</td>
<td>$C$ hispidium</td>
<td>1.00</td>
<td>2.91</td>
<td>0.67</td>
<td>0.83</td>
<td>0.02</td>
<td>1.09</td>
<td>0.74</td>
</tr>
<tr>
<td>05</td>
<td>$B$. verticulata</td>
<td>1.76</td>
<td>0.05</td>
<td>0.78</td>
<td>1.24</td>
<td>BDL</td>
<td>1.21</td>
<td>0.05</td>
</tr>
<tr>
<td>06</td>
<td>$U$ lobata</td>
<td>0.84</td>
<td>BDL</td>
<td>1.46</td>
<td>0.94</td>
<td>BDL</td>
<td>1.16</td>
<td>0.08</td>
</tr>
<tr>
<td>07</td>
<td>$A$ gayyannus</td>
<td>1.29</td>
<td>0.03</td>
<td>0.75</td>
<td>1.49</td>
<td>BDL</td>
<td>0.53</td>
<td>1.67</td>
</tr>
<tr>
<td>08</td>
<td>$E$ trenuda</td>
<td>0.49</td>
<td>0.07</td>
<td>1.81</td>
<td>0.42</td>
<td>0.08</td>
<td>1.56</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Key: BDL = Below Detectible Limit

Concentration of heavy metals ($Pb$, $Cu$, $Zn$, $Mn$, $Ni$, $Cr$, and $Cd$) in plant tissues of the shooting range i.e. shoots and roots separated are shown in Fig. 2. As shown by the data, the metal concentrations among the species at shooting range differed, indicating their different capacities for metal uptake.

$A$ zygia accumulated a significantly higher $Pb$ (12.30 mg/kg$^{-1}_{shoot}$ and 8.71 mg/kg$^{-1}_{root}$) compared to others species and metals. Also $V$. paradoxa accumulated higher $Pb$ (11.01 mg/kg$^{-1}_{shoot}$ and 9.02 mg/ kg$^{-1}_{root}$) than other metals. Accumulation of $Pb$ in the tissues of other species was comparatively higher than the other metals. The lowest accumulated metal was
Ni in *C. hispidium* (0.02 mg/kg\(^{-1}\) root). Out of the 8 plant species *A. gayyamus* only had the highest concentration of Ni (0.11 mg/kg\(^{-1}\) root) which was below detectable limit (BDL) in most of the species such as *A. zygia*, *V. Paradoxa*, *B. verticulata* etc. Translocation factor, ratio of the metal content in shoot to root, showed the occurrence of internal metal transportation. The data as presented in Table 3 clearly indicate that metals accumulated by the sampled plant species were significantly retained in the roots. \((T_F < 1)\). This is evident in most of the species, except in some such as *A. zygia*, *V. paradoxa*, *I. doka*, *C. hispidium*, *B. verticulata*, *A. gayyamus* for Pb \((T_F = 1.41, 1.22, 1.01, 1.00, 1.76\) and 1.29 respectively); *I. doka*, *C. hispidium* for Cu \((T_F = 1.01\) and 2.91 respectively); *A. zygia*, *V. paradoxa*, *U. lobata* and *E. trenuela* for Zn \((T_F = 1.49, 1.21, 1.46\) and 1.81 respectively); *A. zygia*, *V. paradoxa*, *I. doka*, *B. verticulata*, *A. gayyamus* for Mn \((T_F = 1.69, 1.31, 1.20, 1.24, 1.49\) respectively); *A. zygia*, *V. paradoxa*, *I. doka*, *C. hispidium*, *B. verticulata*, *U. lobata* and *E. trenuela*, for Cr \((T_F = 1.31, 1.17, 1.10, 1.09, 1.21, 1.16,\) and 1.56 respectively); and *A. gayyamus* for Cd (1.67).

### Concentrations of Metals in the Sampled Plants of Unpolluted Sites

![Graph showing concentrations of Pb and Cu in sampled plants](image-url)
The 8 studied plant species were also collected from the unpolluted site (control) located 20 km away from the studied or (polluted) site.

Generally, the concentrations of metals in the plants from the polluted site were higher than the unpolluted site. Although species for the polluted and unpolluted site were the same, the physicochemical parameters in their substrata were remarkably differed.

Figs. 2. Concentration of metals in plant species of polluted and unpolluted site
5. DISCUSSIONS AND CONCLUSION

Concentration of Metals and Tolerance in Plants Species

The present study actually shows higher concentration of metals in the soils of the shooting range than in the soils of a neutral control site, an indication of occurrence of pollution. The concentration of Pb, Mn, Cr, Cd and Zn were significantly higher in soil samples of the polluted site than unpolluted site. Out of the seven metals detected, the mean concentrations of Pb were higher compare to other metals. This conforms to the report of Ronney et al (1999), that new bullets and pellets contain higher percentage (90%) of Pb than most of the other metals. The results of physico-chemical parameters, pH, EC, N and water holding capacity were suggestive of the fact that they were suitable for metal up take by plants. The data on concentrations of metals in plant species of the polluted site were significantly higher than those of the unpolluted site.

In general, the sampled plant species differed widely in their ability to absorb and accumulate metals. Concentrations in the root tissues were higher than in the shoot. This indicates greater availability of the substrate metals in the root as well as limited interior mobility of the ions in the plants a factor that depends on the plant-water relationship, solute and pressure potentials, agreeing with the earlier reports of Taylor (1998); Outridge and Noller (1991) and Fitzgerald et al., (2003). Concentrations of metals in the root of plants from polluted site were higher in most of the studied species than the other.

The concentration of metals in the plant tissues usually depends on their concentrations or level of availability in the soil (Istivan and Benton, 1997). Therefore, the result of metal concentration in the present study suggests that heavy metals tolerating strategy is widely evolved among different plant species and is usually observed in species that grown in metal contaminated area (Gries and Garbe, 1989).

The results of the translocation factors are according to the species uptake abilities and essentially the relationship between the concentrations of the metals in shoot and roots (Nouri et al., 2009). Although the T_F in plant species of the polluted site were significantly higher (T_F >1) than those of the control site, metals were accumulated more in the roots than the shoots (Outridge and Noller, 1991).

Use of plant Species in Phytoremediation

Phytoremediation is the use of green plants to ‘clean up’ environmental pollutants or render them harmless (Cumingham and Berti, 1993). Is a feasible practice for military sites. Depending on the differences in the capacities of metal uptake any species, regardless of its group- tree, shrubs, herb or grass with the transformation factor greater than 1 (T_F >1), could be used as potential phytoremediator (Nouri et al., 2009). As shown by the result of present study, A zgyia, I doka, C hispidium, B verticulata, E trenuda etc. could be selected as very good candidates for phytoremediation. Therefore the purpose of this study was to screen plants growing on the polluted site to primarily determine their potential for metal uptake and accumulation. Therefore the result of the present study is indicative of the fact that most of the 8 plant species can grow on heavy contaminated sites, absorbing a wide range of heavy metals in the soil and not being affected by high concentrations of the metals and also possess capabilities for metal tolerance and resistance than the more sensitive species.

Occurrence of metal concentration higher than toxic level in some species suggested that the process of internal metal detoxification might also exist, thus they can be effectively
used for phytoremediation. The result also suggest that plant-soil interaction should be considered when selecting plant species and also in the development of any phytoremediation technique.

References


