Nigerian Journal of Ecology (2022) 18(2): 49-61

ISSN: 1116-753X (Print); E-ISSN: 2955-084X (Online)

Assessment of Heavy Metal Composition of Plants Growing in Recycled Metal Slag Polluted Soils in Ogijo, Ogun State

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(Accepted 17 December, 2022)

ABSTRACT

Soils of slag deposited waste dumpsites contain significant amounts of heavy metals, which difficult to remove from the environment. In recent years, metal pollution of the environment has increased especially in long term metal recycling facilities. This study assessed concentrations of heavy metals in soil and plants in a slag dumpsite in Ogijo, Ogun state and their comparative hyper-accumulator capacity. A 10 m by 50 m area was measured from base of a large slag heap in the study area. Slag samples were randomly collected from slag heap, soil samples were collected at the base of the heap (0 m) and at 50 m from the base. Mature whole samples of *Chromolaena odorata, Alternanthera sessilis* and *Megathyrsus maximus* were collected at 0 m, 10 m and 50 m from the base of heap. All samples were collected in three replicates and analysed for Cu, Fe, Zn, Mn, Pb, Ni, Cd and Cr. Data obtained were analysed with ANOVA, mean separation was done using Duncan's Multiple range test at $P \leq .05$. Results obtained (in mg/kg) showed significant differences ($P \leq .05$) in all metals tested except in Ni, Cd and Cr that were below detectable limits. Lowest mean parameters (mg/kg), except Zn were observed in plant samples. Mean Cu, Fe and Pb were significantly highest ($P \leq .05$) in slag with values 81.93±14.19, 421.61±71.94 and 48.73±2.52 respectively, Mn in soil at 0 m with mean value 4.30±0.26 and Zn in *C. odorata* with a mean of 52.88±5.41. In soil, highest mean concentrations were obtained, except Cu which occurred at 0 m, but not significantly different from those at 50 m. Among plants tested, lowest mean values of Cu (1.31±0.70), Fe (104.59±6.88) and Pb (0.61±0.26) occurred in *A. Sessilis*, Zn (7.50±0.98) in *M. maximus* and Mn (1.02±0.46) in *C odorata.* Highest mean Cu, Fe, Mn and Pb were recorded in *M. maximus,* with values 30.01±12.01, 255.60±21, 4.28±0.66, and 4.96±1.40 respectively, while Zn (52.88±5.41) occurred in *C. odorata*. Among the three plants, *Megathyrsus maximus* had the highest hyperaccumulator potential, and therefore is the most suitable plant for phytoremediation of heavy metal from polluted soils.

Keywords: Phytoremediation, Hyperaccumulator, Soil pollution, Invasive weeds, Scrap metal,

INTRODUCTION

Pollution of the natural environment by heavy metals have become a serious problem, because, these metals are non-biodegradable (Gautam *et al*., 2016; Ashraf *et al*., 2019). In addition, most of them have toxic effects on living organisms, when they exceed a certain concentration (Ghrefat and Yusuf, 2006). Although certain metallic elements are required by plants and animals in very small quantities for some physiological processes (WHO, 1996; Hall, 2012), high levels of these elements can become harmful to living organisms ((Uzondu, 2012; Turkdogan *et al.*, 2013). Metals display some cytotoxicity and genotoxicity in both plant animal and (Ciriaková, 2019; Saravanan *et al*., 2021). Nickel and lead have been reported to produce chromosomal aberrations in *Allium sativum* (garlic) (Sarac *et al*., 2019), while Lead and cadmium are cytotoxic to human bone (Al-Ghafari *et al*., 2019). Pollution by heavy metals may occur through natural or anthropogenic sources. However, pollution by anthropogenic sources is the most widespread (Nazir *et al.,* 2015). The contribution of metals from industrial, agricultural and mining processes, domestic effluent discharges, solid waste disposal and automobile and other atmospheric emissions from industrial establishments are some of the major sources of environmental pollution (Kapungwe, 2013; Rafique and Tariq, 2016; Onder *et al.*, 2017, Tejaswini *et al*., 2022).

Metal recycling activities are a particularly important source of heavy metal contamination, causing negative impacts on the surrounding environment (Uzondu, 2012). The production of iron and steel from scrap iron and steel metal recycling industries yields large amounts of slag as by-products (Gunn, 2015). This slag generally contains a considerable amount of heavy metals, which, through indiscriminate disposal, makes it one of the main sources of heavy metal pollution in the environment (Beauman, 2017). Iron and steel slag are widespread in Nigeria because the industries producing these by-products are found in the north, south, west and eastern parts of the country (Elijah, 2013). Slag production in Nigeria from this source is estimated at 0.29 tonness per tonne of steel produced. Therefore, the total estimated production of iron and steel slag in Nigeria is 0.55405 million tonnes per year (Uzondu, 2012). Consequently, recycle iron waste and slag are pollutants, which litters some cities and towns in Nigeria (Uzondu, 2012).

Slag is usually a mixture of metal oxides and silicon dioxide and can contain metal sulfides and elemental metals. According to Luxan *et al.* (2010), the major components of these slags include the oxides of calcium, magnesium, silicon and iron, with lesser amounts of magnesium, phosphorus, and others depending on the specifics of the raw materials used. Leaching concerns are typically towards non-ferrous or base metal slags, which tend to have higher concentrations of potentially toxic elements (PTEs), but ferrous and ferroalloy slags may also have them. In recent times, slags are usually transported along with slag tailings to slag dumps. Here, they are exposed to weathering, which generates concerns about leaching of PTEs and hyper-alkaline runoffs into the soil and water, thereby, endangering the local ecological communities (Potysz *et al.,* 2018; Ettler and Kierczak, 2021). Soils in and around slag deposited waste dumpsites have been reported to contain a significant amount of heavy metals (Ukpebor and Unuigbe, 2013).

Characteristics of heavy metals make them persistent and sometimes difficult to remove from the environment. Currently, several alternative technologies are used to treat environmental heavy metal contamination and these comprise chemical, physical and biological treatments. Most physical and chemical methods are expensive and do not make the soil suitable for plant growth (Marques *et al*, 2009; Li *et al*., 2019; Dhaliwa *et al.,* 2019). Biological approach or bioremediation on the other hand is an economical and environmentally friendly approach (Dhaliwa *et al.,* 2019), because it is achieved through natural processes and encourages the establishment or reestablishment of plants on polluted soils.

Phytoremediation is an aspect of bioremediation that uses plants for the treatment of polluted soils (Luxan *et al.*, 2010; Gonzalez and Gonzalez-Chavez, 2016). It involves the use of natural hyperaccumulators, which are plants with very high metal-accumulating ability. Hyperaccumulators accumulate 10 to 500 times more metals than ordinary plant (Chaney *et al.,* 1997); hence, they are very suitable for phytoremediation. An important characteristic which makes hyperaccumulation possible is the tolerance of these plants to increasing concentrations of these metals.

Plant communities in soils contaminated with heavy metals respond differently to the presence of heavy metals in the soil. Heavy metals generally produce common toxic effects on plants, such as low biomass accumulation, chlorosis, inhibition of growth and photosynthesis, altered water balance and nutrient assimilation, and senescence, which ultimately cause plant death (Friedlova, 2010; Turkdogan *et al.,* 2013). Most plants are sensitive to the contaminant even at very low concentrations, while some have developed resistance, either by excluding or accumulating the contaminant (Chaudhry *et al.,* 2008). Works have shown that some common plants have ability of accumulating high level of heavy metals from the soil (El-Sharabasy and Ibrahim, 2010; Zheng *et al.*, 2017). Therefore, whenever a plant species is identified to have capacities to remediate elevated concentrations of heavy metals in the environment, emphases are usually on how to maximize its remediation abilities (Omoregie *et al.,* 2019). On this basis, it was therefore important in this research to assess concentration of heavy metals in plants and determine their hyper-accumulator potentials. This study was conducted in a slag dump in Ogijo, Ogun state, to assess heavy metals concentration in slag and soil and compare their accumulation in selected plants growing in the dumpsite.

METHODOLOGY

Description of study location

This study was conducted in slag dumpsite in Ogijo, Ogun state. Ogijo is a town in Ogun state that shares its boundary with Lagos state. It is an industrial area, among whom most recent industries have been the scrap metal recycling factories. Evidence of pollution by these factories is obvious in their immediate surroundings and extends far beyond their vicinities into neighbouring areas. Among these are untreated waste slags generated as by-products of scrap metal recycling process, often deposited indiscriminately in heaps on the soil surface (Plate 1). One of such slag dumpsites was used in this study. The site is located on latitude 60 43’47’’N; longitude 30 31’35”E and 68.9 feet (21 m) above sea level.

Plate 1. The study location showing slag heap (A) and surrounding vegetation (B) (arowed)

Collection of samples

A preliminary survey of site was conducted prior to sample collection. An area of 10 m by 50 m was measured from the base of a large slag heap in the study area. Samples of slag were randomly collected from slag heap; soil samples were collected from the base of the heap (0 m) and at 50 m from the heap. Three plant species; *Chromolaena odorata* (L.) R.M.King & Robinson, *Alternanthera sessilis* (L.) R.Br. ex DC and *Megathyrsus maximus* (Jacq.) B. K. Simon & S. W. L. Jacobs; were selected on the basis of their availability and abundance in the study location. Mature whole plant samples were collected at approximately at 0 m, 10 m and 50 m from the base of heap. All samples were collected in three replicates and 50 g of each was analysed for; Cu, Fe, Zn, Mn, Pb, Ni, Cd and Cr.

Sample preparation and analysis

All samples were analyzed for heavy metals analytical methods adopted by Association of Official Analytical Chemists (AOAC) 2005. Slag samples were crushed to fine particles. Both soil and crushed slag samples were air dried and sieved with a 2 mm sieve. Plant samples were washed in clean water to remove external impurities. Dry ashing digestion was performed, following the procedure recommended by (Issac and Kerber, (1971).

Heavy Metal Determination

The metals were determined on filtrate of sample digested by atomic absorption spectrometry. Test results were validated with calibration curves obtained with certified metal standards. Calibration standard were prepared from stock by applying dilution formula $C_1V_1 = C_2V_2$ to obtain working range.

Dilution factor (DF) was expressed as:

$$C1/C2 = V1/V2.$$

Where, C1 = concentration of stock solution, C2 = concentration of diluted solution, V1 = initial volume removed from the stock solution and V2 = volume of final diluted solution. Thus,

$$Dilution\ Factor = final\ solution\ volume / volume\ of\ stock\ solution\ \ldots.1$$

Quantitation of metal levels in the soil samples was determined with Perkin Elmer Win Lab AA software. Levels were converted from mg/1 to mg/kg by the following formula:

$$Conc.\ of\ metals\ in\ mg/kg = Conc.\ in\ mg/L\ X\ Dilution\ Factor\ X\ volume\ of\ digest / weight\ of\ sample\ digested\ \ldots.\ 2$$

Statistical analysis of data

Data obtained were subjected to Analysis of Variance (ANOVA) using the statistical package for the social sciences (SPSS) 25.0 software. Mean separation was carried out by Duncan’s Multiple range test (DMRT) at $P \leq .05$. In every parameter analysed, results obtained were mean values from three replicates.

RESULTS

Results obtained from concentration of heavy metals (in mg/kg) in slag, soil and plants are presented in Table 1. Results showed that Ni, Cd and Cr that were below detectable limits in all samples tested. However, there were significant differences ($P \leq .05$) in all other metals tested which were; Cu, Fe, Pb, Mn and Zn.

Results showed that mean Cu, Fe and Pb were significantly higher ($P \leq .05$) in slag compared to all other samples, with values 81.93±14.19, 421.61±71.94 and 48.73±2.52 respectively, while highest Zn and Mn occurred in *C. odorata* and soil at 0 m, with mean values 52.88±5.41 and 4.30±0.26 respectively, although, concentration of Mn at this point was not significantly different from those in other samples except in *C. odorata* at 10 m.

In soil, highest mean for all metals, except Cu, occurred in 0 m, though not significantly different ($P \geq .05$) from those at 50 m. Mean values in soil at 0 m and 50 m respectively were: Cu: 6.96±0.35 and 7.10±0.34; Fe: 220.39±3.19 and 218.09±2.65, Zn: 32.37±1.56 and 30.98±1.17; Mn 4.30±0.26. and 3.48±0.32; Pb: 3.68±0.34 and 3.61±0.21.

In plants, lowest mean values for Cu (1.31±0.70), Fe (104.59±6.88) and Pb (0.61±0.26) occurred in *A. Sessilis*, Zn (7.50±0.98) in *M. maximus* and Mn (1.02±0.46) in *C odorata.* Highest mean values for Cu, Fe, Mn and Pb in plants were recorded in *M maximus*, with mean values 30.01±12.01, 255.60±21, 4.28±0.66, and 4.96±1.40 respectively, while Zn occurred in *C. odorata* with a mean value of 52.88±5.41.

Lowest mean Cu (1.31±0.70) occurred in *Alternanthera sessilis* at 10 m, but was only significantly lower ($P \leq .05$) mean concentration in slag samples and M. maximus at 10 m.

Mean Cu was significantly highest ($P \leq .05$) in slag (81.93±14.19) compared to other samples. This was followed by mean concentration in *M. maximus* at 10 m from the heap, with mean value of 30.01±12.01, which was also significantly higher ($P \leq .05$) than all samples except in *M. maximus* at 50 m with a mean value of 15.72±9.27 (Table 1).

Mean concentration Fe followed nearly a similar pattern to that of Cu. Mean Fe (104.59±6.88) was also lowest in *A. sessilis*, but at 0 m (Table 1). The value was not significantly higher ($P \geq .05$) than all other samples except in slag (421.61±71.94) and *M. maximus* at 0 m (255.60±21.36). Mean concentration in slag was significantly higher ($P \leq .05$) than that found in all samples, and similarly was followed by that present in *M. Maximus* at 0 m. However, mean concentration in *M maximus* was not significantly higher ($P \leq .05$) than that found in all soil and *C. odorata* samples at all distances from slag heap.

Concentration of Pb in samples followed the exact pattern as those observed in Fe. Lowest and significantly highest ($P \leq .05$) mean Pb occurred in *A. sessilis* at 10 m with a mean value of 0.61±0.26 and in slag with mean value of 48.73±2.52 respectively (Table 1). Highest concentration was followed by that found in *A maximus* at 0 m, which had a mean value of 4.96±1.40, which was not significantly different ($P \geq .05$) from mean concentration of Pb in all samples except the lowest and highest mean values recorded in *A. sessilis* and slag as mentioned earlier (Table 1).

In Mn, lowest mean value of 1.02±0.46 occurred in *C. odorata* at 10 m. Results further showed that lowest mean value was not significantly ($P \geq .05$) lower than all samples except in soil at 0 m (4.30±0.26) and 50 m (3.48±0.32), *A maximus* at 0 m (4.28±0.66) and *A. sessilis* at 10 m

(3.35±0.78). Highest mean Mn occurred in soil at 0 m with a value of 4.30±0.26 (Table 1).

Results obtained for concentration of Zn in samples are also shown in Table 1. Lowest mean Zn occurred in tissues of *M. maximus* at 10 m (7.50±0.98) This was however not significantly different (*P* ≥ *.05*) from its concentration in slag (11.30±1.92), *M. maximus* at 50 m (23.50±7.29), *A. sessilis* at 50 m (23.37±3.12) and *C odorata* at 0 m (8.15±0.98) and 10 m (8.01±0.83) (Table 1). Highest mean Zn was found in *C. odorata* at 50 m with concentration of 52.88±5.4 which was significantly higher (*P* ≤ *.05*) than those in all other samples tested. This was followed by that in *A. sessilis* with a mean value of 36.48±8.43 (Table 1).

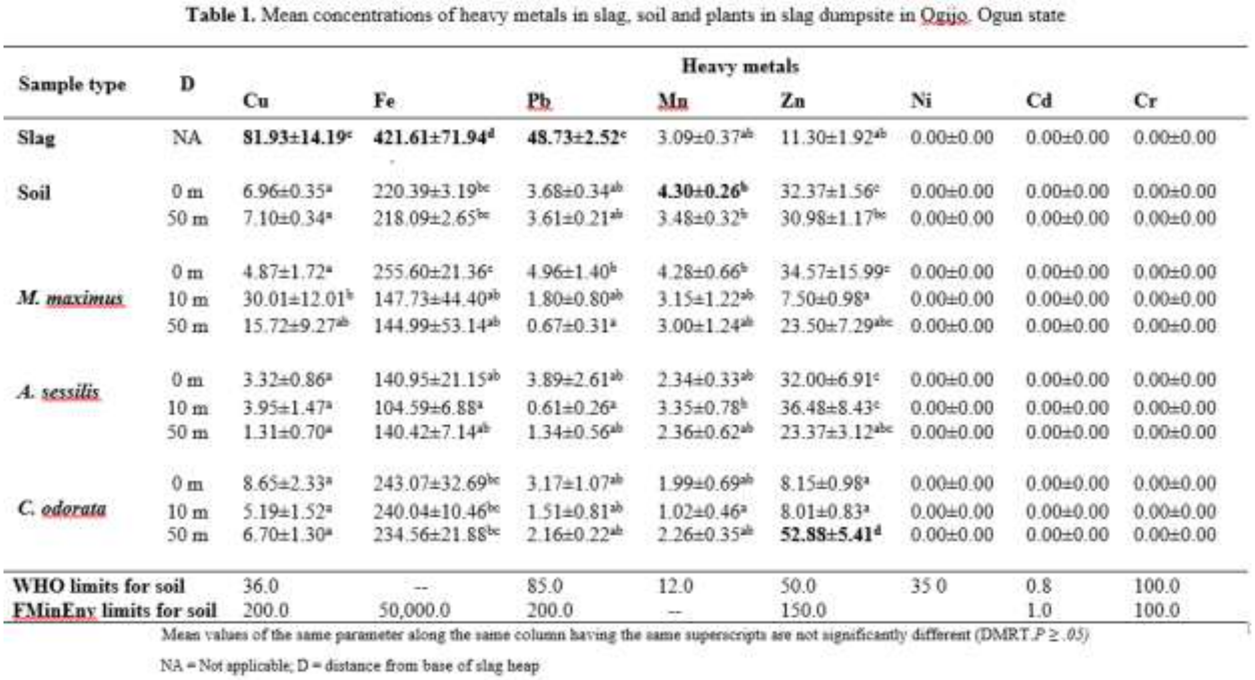

Table 1. Mean concentrations of heavy metals in slag, soil and plants in slag dumpsite in Ogijo, Ogun state

Sample type	D	Heavy metals							
		Cu	**Fe**	**Pb**	**Mn**	**Zn**	**Ni**	**Cd**	**Cr**
Slag	NA	**81.93±14.19^{c}**	**421.61±71.94^{d}**	**48.73±2.52^{c}**	3.09±0.37^{ab}	11.30±1.92^{ab}	0.00±0.00	0.00±0.00	0.00±0.00
Soil	0 m	6.96±0.35^{a}	220.39±3.19^{bc}	3.68±0.34^{ab}	**4.30±0.26^{b}**	32.37±1.56^{c}	0.00±0.00	0.00±0.00	0.00±0.00
	50 m	7.10±0.34^{a}	218.09±2.65^{bc}	3.61±0.21^{ab}	3.48±0.32^{b}	30.98±1.17^{bc}	0.00±0.00	0.00±0.00	0.00±0.00
M. maximus	0 m	4.87±1.72^{a}	255.60±21.36^{c}	4.96±1.40^{b}	4.28±0.66^{b}	34.57±15.99^{c}	0.00±0.00	0.00±0.00	0.00±0.00
	10 m	30.01±12.01^{b}	147.73±44.40^{ab}	1.80±0.80^{ab}	3.15±1.22^{ab}	7.50±0.98^{a}	0.00±0.00	0.00±0.00	0.00±0.00
	50 m	15.72±9.27^{ab}	144.99±53.14^{ab}	0.67±0.31^{a}	3.00±1.24^{ab}	23.50±7.29^{abc}	0.00±0.00	0.00±0.00	0.00±0.00
A. sessilis	0 m	3.32±0.86^{a}	140.95±21.15^{ab}	3.89±2.61^{ab}	2.34±0.33^{ab}	32.00±6.91^{c}	0.00±0.00	0.00±0.00	0.00±0.00
	10 m	3.95±1.47^{a}	104.59±6.88^{a}	0.61±0.26^{a}	3.35±0.78^{b}	36.48±8.43^{c}	0.00±0.00	0.00±0.00	0.00±0.00
	50 m	1.31±0.70^{a}	140.42±7.14^{ab}	1.34±0.56^{ab}	2.36±0.62^{ab}	23.37±3.12^{abc}	0.00±0.00	0.00±0.00	0.00±0.00
C. odorata	0 m	8.65±2.33^{a}	243.07±32.69^{bc}	3.17±1.07^{ab}	1.99±0.69^{ab}	8.15±0.98^{a}	0.00±0.00	0.00±0.00	0.00±0.00
	10 m	5.19±1.52^{a}	240.04±10.46^{bc}	1.51±0.81^{ab}	1.02±0.46^{a}	8.01±0.83^{a}	0.00±0.00	0.00±0.00	0.00±0.00
	50 m	6.70±1.30^{a}	234.56±21.88^{bc}	2.16±0.22^{ab}	2.26±0.35^{ab}	**52.88±5.41^{d}**	0.00±0.00	0.00±0.00	0.00±0.00
WHO limits for soil		36.0	--	85.0	12.0	50.0	35 0	0.8	100.0
FMinEnv limits for soil		200.0	50,000.0	200.0	--	150.0		1.0	100.0

Mean values of the same parameter along the same column having the same superscripts are not significantly different (DMRT *P* ≥ *.05)*

NA = Not applicable; D = distance from base of slag heap

DISCUSSION

Metal recycling continues to grow globally due to increasing awareness of resource conservation and economic benefits (Anderson *et al*., 2017). However, the process usually results in generation of heavy metal contaminated liquid and solid slag wastes. Through indiscriminate disposal of these wastes, metal recycling facilities discharge variety of heavy metals into the environment. Common examples of heavy metals that have been reported include lead, aluminium, arsenic, chromium, manganese cadmium, nickel, copper, and zinc are also released by the facilities (Beauman, 2017; O'Connor *et al*., 2019). This agrees with the results from the present study where high levels of heavy metals including iron, lead, copper, manganese, nickel and zinc were observed in samples of slag waste deposited by metal recycling factories in the study area.

Several reports have shown that presence of heavy metal contaminated slag in the environment can lead to heavy metal contamination of immediate soil of the areas

(Ettler, and Vítkova, 2021; Ettler, and Kierczak, 2021). Comparing concentration of heavy metal in slag and soil samples at different distances from slag waste deposits, showed that higher concentration of most heavy metals were recorded in slag, followed by soil and plants nearest to slag heap, with much less concentrations in soils located at a reasonably far distant from the slag heap which follows a pattern previously described by Ogundele *et al*. (2015). It can therefore be inferred that slag waste is the source of heavy metal pollution of soil in the study site. This agrees with earlier report that slags transported along with slag tailings to slag dumps, where they are exposed to weathering, may result in leaching of potentially toxic elements (PTEs) such as heavy metals and hyper-alkaline runoffs into the soil and water, endangering the local ecological communities (Potysz *et al.*, 2018; Ettler and Kierczak, 2021). Thus, heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem (McLaughlin *et al*., 2011). Contamination of biota and groundwater with potentially toxic heavy metals also has important implications for human health (Slaveykova and Cheloni, 2018).

Reports have shown that plants growing in heavy metal-contaminated sites generally accumulate higher amounts of heavy metals in their edible and non-edible parts, at quantities high enough to cause clinical problems to both plants, animals and human beings (Uzondu, 2012; Ogundiran and Osibanjo, 2018). This agrees with results obtained in this study, where high concentration of heavy metals was present in all plants samples growing in metal contaminated soil of the study area, especially those plants growing nearer to the source of contamination. Through this mechanism, heavy metals in soil can accumulate in vegetables, which can be transferred to other media through the food chain (Wang *et al.*, 2017). Although heavy metal accumulation in edible plants can pose threat to health of plant and animals, the mechanism has been exploited in environmental remediation for removal of pollutants from different environmental media through a process of phytoremediation.

Plants have an advantage growing on metal contaminated soil. Such plants can withstand high accumulation of metals in their aerial tissues (Vesk and Reichman, 2019) and can also eliminate competitive plants (Maestri *et al.*, 2010). These are attributes common to invasive alien plants and agree with those of the three plants selected for this study. These three were the most widespread dominant plants species in the study site. Invasive species are non-native species that have become established in a new region, devoid of natural enemies (Reichard and White, 2001; Fountain, 2016). Such plants are characteristically adaptable, aggressive and have a high reproductive capacity, having escaped natural enemies and herbivores and have dominated native plants through several mechanisms resulting in outbreak of their populations (Florida Exotic Pest Plant Council, 2007). Invasion by all three plants; *C. odorata, A. sessilis* and *M. maximus;* have been reported (Fan *et al.*, 2013; PIER, 2013; Uyi *et al*. 2013; *C. odorata* and *A. sessilis* are also listed in Global Invasive Species Database (GISD, 2023) as serious invasive weeds in many parts of the world, while *M. maximus* is reported as a highly successful invader in tropical and warm temperate areas (Rojas-Sandoval and Acevedo-Rodríguez, 2013).

In this study, High levels mean concentration of heavy metals including Cu, Fe, Mn and Pb in plants were recorded in *M maximus,* showing higher accumulation of metals compared to *C. odorata* and *A.*

sessilis. However, a study has shown that obvious signs of phyto-toxicity appeared in *M maximus* plants exposed to 120 ppm Pb^{2+} and Cd^{2+}, suggesting that the plant may be a moderate metal accumulator (Olatunji *et al*., 2014). *Chromolaena odorata* showed less metal accumulation capacity except for Zn in the present study. A study on the remediating capacity of different plants showed that *C. odorata* still thrived under heavy metal induced stress, that resulted in disruption of physiological functions and caused morphological deficiencies in other plants (Ciriakova, 2019). *Alternanthera sessilis* leaves are rich in protein and are eaten raw as a fresh green leafy vegetable in many countries of South Asia (Alveera *et al.,* 2009). It has been reported that *A. sessilis* has a potential to hyperaccumulate Cd in the leaves (Alveera *et al.,* 2009). In the present study, Cd was not detected in the soil to verify this claim. However, accumulation of heavy metals in *A. sessilis* was lowest among the three plants, indicating significant reduction in the potential risk of the plant to humans on consumption. Higher accumulation of Zn in *C. odorata* at 50 m from slag heap was observes in the present study. Zinc is one of the most mobile heavy metals in surface waters and groundwater. In addition, zinc readily precipitates under reducing conditions and in highly polluted systems, when it is present at very high concentrations, and may co-precipitate with hydrous oxides of iron or Magnesium (Evanko and Dzomback, 1997). Therefore, the highly mobile nature of the metal may have accounted for rapid leaching and movement from the source, causing higher concentration at a point remotely located from the source of pollution.

CONCLUSION

Although all three plants accumulated heavy metals in their tissues, *Megathyrsus maximus* had the highest heavy metal accumulation potential in all heavy metals assessed except Zn, with *Chromolaena odorata* having highest accumulation capacity for Zn while *Alternanthera sessilis* showed the least potential for heavy metals accumulation. Therefore, among the three plants, *Megathyrsus maximus* is the most suitable plant species for the phytoremediation of heavy metals from polluted soils with regard to heavy metals tested in the present study.

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