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ASSESSMENT OF METAL ACCUMULATION IN PLANT AND SOIL AT EGGON COMMUNITY MINING SITE, NASARAWA, NIGERIA

[1,2]Ilyas, S., [3]Sabo, A. and [1*]Akomolafe G. F.

[1]Department of Plant Science and Biotechnology, Federal University of Lafia, PMB 146, Lafia, Nasarawa State, Nigeria
[2]Department of Biology, Federal University of Technology Owerri, PMB 1526, Owerri, Nigeria
[3]Department of Environmental Management Technology, Abubakar Tafawa Balewa University, PMB 0248, Bauchi State, Nigeria.

[*]**Corresponding author:** *gbenga.akomolafe@science.fulafia.edu.ng*

ABSTRACT
The extent of soil contamination by heavy metals and the potentials of herbaceous plant species to remediate the soils at a selected mining site in Nasarawa state were assessed. Herbaceous plants and their associated soils were collected from Eggon community mining site in Nasarawa State, Nigeria. There was a generally higher concentration of the heavy metals in most of the plants than in soils which indicates the ability of the plant to tolerate and accumulate these metals. None of the collected plants attained the status of hyperaccumulator. However, most of the plants have potentials of been a phytostabilizer or phytoextractor. At the mining site, *Pseudognaphalium luteo* and *Cyperus rotundus* were observed to be the phytoextractor and phytostabilizer of Lead respectively. These same two plants could also extract Copper, whereas *Eclipta alba* was identified as a phytoextractor of Manganesse. Also, *Pseudognaphalium luteo, Physalis minima, Cyperus rotundus, and Sphenoclea zeylancia* were observed as phytostabilizers of the metal.

Keywords: Eggon, Heavy metals, Mining, Phytoremediation.

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INTRODUCTION
Heavy Metal accumulation in plants has multiple direct and indirect effects on plants growth and can alter many physiological functions by forming complexes with O, N and S ligands. They also interfere with membrane functioning, water relations, protein metabolism and seed germination (Hassan *et al.*, 2009). Impediment of proper absorption and essential element transport in plants, metabolic alterations and inhibition of adequate growth, reproductive alterations, wilting, chlorosis, dehydration, mortality and photosynthesis inhibition are among the main reported effects on plants due to heavy metal exposures (Cheng, 2003; Eisler, 1998; Efroymson *et al.*, 1997).

The overall effect of mining activities on plant communities has led to the presence of different concentration levels of metals such as Cd, Cu, Se and Zn in soil and water and as well causes a reduction in the diversity and abundance in plant communities. (Kashem & Singh, 1999; Peplow, 1999). Mining operations completely alter a site ecosystem by disrupting the ecological balance, natural landscapes, agricultural lands, forest plantation and vegetation as well as the economic food and tree crops.

The selected mining sites have undergone severe land degradation leading to loss of aesthetic land value, fertility of the land and soil erosion. Also, the use of artisinal means of mining has further exposed the land to heavy metal toxicity as well as endangering the habitants of these places as there is a tendency for the metals to accumulate in food crops grown close to such places. The increasing discharge of heavy metals to the environment due to mining activities is posing serious threats to the soils, water and health of people in these areas. Therefore, this study is aimed at assessing metal accumulation in plant species growing on soil in a mining site at Eggon community in Nasarawa state, with a view to determining their phytoremediation potentials.

MATERIALS AND METHODS

Study Area

The mining site is located in Nasarawa Eggon local government area (LGA). The area has a tropical savannah climate with two marked seasons, wet and dry that is suitable for cultivation of varieties of crops. It has a mean temperature of 15.6^{0}C and 26.7^{0}C, with an annual rainfall between 1317mm and 1450mm, it rains April to October. It has a population density of 166.5/km^2. The vegetation is composed mainly of grasses and isolated trees, some of the trees of economic value that are found include the Shea Butter Tree *(Vitelaria paradoxa*), Locust Bean Tree *(Parkia biglobosa*) amongst others. This particular mining site is known for extracting Galena ore from the Earth crust. It is a natural mineral form of lead (II)sulfide. It is the most important ore of lead, an important source of silver. It is often well crystallized, and forms in many interesting and distinct crystal shapes. Galena is a gray, cubic, shiny dense mineral most commonly associated with Lead. The site has a coordinate of Latitude 08^o 41` 564``N and Longitude 08$^o$ 33` 727``E with an elevation of 283M (Figure 1).

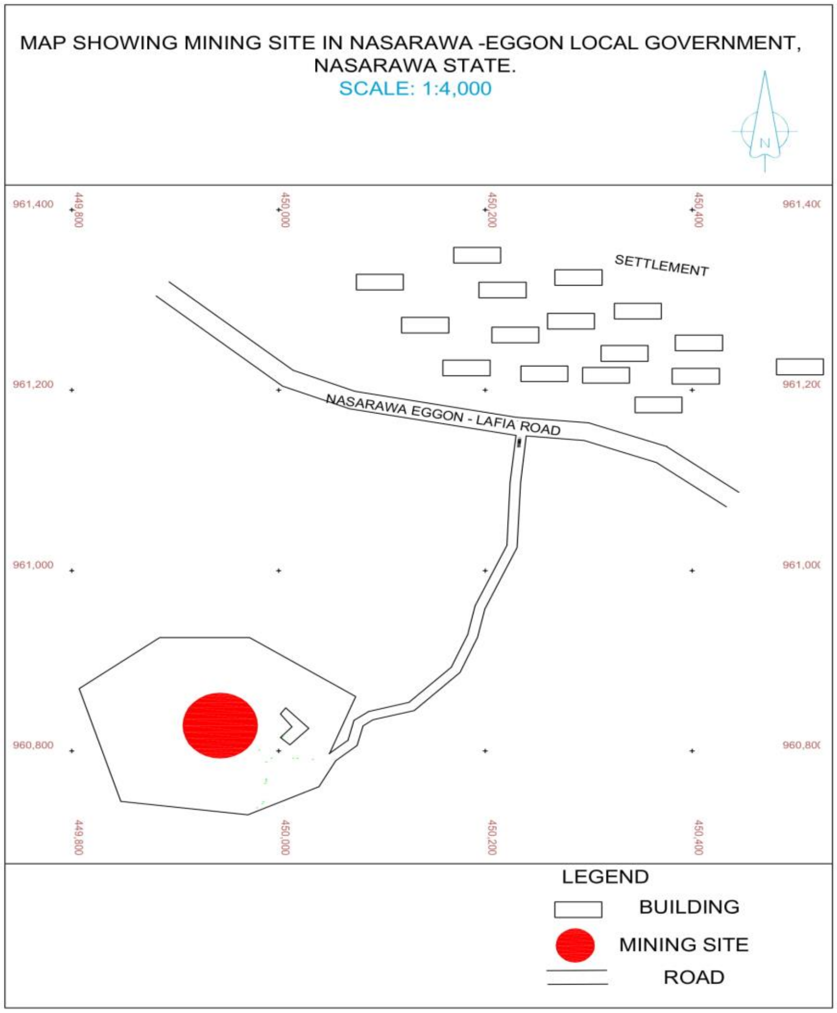

Figure 1: Map showing mining site at Eggon community

Sample collection

Fresh plant samples were carefully uprooted from the sampling areas to avoid any damage to the plant parts. The sampling areas were marked using a measuring tape starting from 0cm, 50cm and 100cm away from the mining location. Three representatives' plant samples were uprooted from each of the marked point and stored in a well labeled polythene bag to be transported to the laboratory. The soil sample around the rhizosphere of each sampled plant was carefully collected using a hand trowel and stored also in a polythene bag for analysis. Five samples of soils were collected at each sampling point.

Determination of Metal Content

Plant samples were carefully separated into portions of leaves, stems, and root. They were washed, placed into an oven for 48 hours until they are dried, and grinded using ceramic mortar and pestle. The respective soil samples were also dried, ground and sieved using a 2mm mesh sieve size. The plant samples were ashed using crucibles and the extraction process was done using Aqua regia solution. The filtrates were stored in glass vials for extraction. The soil samples were extracted using Mehlich -3 extracting solution. Soil pH was determined in water and also in 1N potassium chloride solution. Organic carbon was determined using Black (1965) potassium dichromate wet oxidation method. Organic matter in the soil was determined according to Black, 1965 as;

%. Organic matter = % Organic Carbon X 1.729 Phosphorus concentrations in both the soil and plants filtrates were determined using the conventional method (Bray and Kurtz, 1984).

The concentration of metals in the filtrates was determined using atomic absorption spectrophotometer, equipped with a digital read out system. Working standards were prepared after serial dilution of 1000ppm metal stock solution in each case. Calibration curves were prepared for the elements individually. A Blank reading was also taken and necessary corrections were made during the calculation of concentration of various elements. The parameters that were investigated include Cd, Cr, Cu, Pb, Mn, Ca, Mg and P.

Determination of Bioconcentration, Translocation and Enrichment factors

Bioconcentration factor (BCF), is defined as the metal concentration in plant root to extractable concentration of the metal in the soil (Danish, 2000). It refers to the ability of the plant body to accumulate the heavy metals from the soil to the roots of the plant. It is expressed mathematically as;

BCF = Croot/Csoil ………. [1]

Where Croot = concentration of metal in root, Csoil = concentration of metal in soil

Translocation Factor (TF) refers to as plant's ability to translocate heavy metal from root to harvestable aerial part (Khan, 2013). When TF > 1 is obtained, it indicates a preferential partitioning of metals from soil to the root and from the root to shoot respectively (Baker and Whiting, 2002). Mathematically, it is expressed as:

TF = Cshoot/Croot ………. [2]

Where Cshoot = Concentration of metal in shoot, Croot = concentration of metal in root

Enrichment factor (EF) is defined as the metal content ratio in shoot to soil. Mathematically, it is expressed as:

EF = Cshoot/ Csoil ………. [3]

Where Cshoot = concentration of metal in shoot, Csoil = concentration of metal in soil

A plant species that has both BCF and TF > 1 has the potential of being used in phytoextraction. If, however only the BCF > 1 and the FT < 1, the species is said to have potential for phytostabilization (Sabo and Ladan, 2004).

Plants capable of accumulating excessive high amount of metal in its above ground part are called hyperaccumulators. Hyperaccumulator are defined as plants that can accumulate > 1000 mg/kg of Fe, Mn, or Zn (Baker and Brooks, 1989).

In addition to this criterion, other authors have included two important attributes associated with hyperaccumulation of heavy metals. According to Baker and Brooks (1989); Market (2003), hyperaccumulator should have metal TF > 1, an important attribute which depicts the ability of the plant to transfer the metal from root to shoot and a mechanism to tolerate excess concentration of the metal in soil. The enrichment factor should also be greater than one (EF >1) which indicates higher concentration of the metal in plant than that in the soil and placing emphasis on the extent of metal uptake by the plants (Mc Grath and Zhao, 2003).

Data Analysis

The differences in soil metal concentrations were determined by one-way ANOVA using the general linear models' procedure (SAS 2004). The comparisons of means were performed using least square difference. The differences in the metal concentrations between the shoots and roots were determined using the Kruskal-wallis non parametric test.

RESULTS

The herbaceous plants recorded in this site are listed in Table 1. At this site, 8 different plants were recorded. *Cyperus rotundus* was identified at two different locations.

A total number of 8 parameters were investigated (Table 2). They include; Cadmium (Cd), Chromium (Cr), Lead (Pb), Copper (Cu), Manganese (Mn), Calcium (Ca), Phosphorus (P) and Magnesium (Mg). The concentrations of the metals in both the root and the shoot were assessed. Cd and Cr were not recorded in any of the plant parts.

Magnesium was also recorded in significant amount in the site. Copper accumulation in plants at the Mining site was highest in the shoot of *Eclipta alba* (3.203 ppm) while its root recorded a concentration of 0.238 ppm. The value in the shoot exceeds the permissible value in plant which is 1.30 ppm (Table 3). Lead concentration was the highest in the roots of *Cyperus rotundus* reaching to 57.946 ppm while the shoot recorded a concentration of 28.439 ppm. The recorded concentration is higher than the allowable limit in plant which is 2 mg/kg. The soil analysis result for the mining site revealed significant differences in the concentration of Calcium and Magnesium at the three locations (Table 4). Calcium and Magnesium showed an observable significant difference. This difference was recorded between the 0cm and other locations. The concentration of metals in soils at the Mining site revealed that, the highest concentration of Pb was recorded in soils of *Sphenoclea zeylancia* reaching up to 200.871 ppm which far exceeds the allowable limit. Its corresponding plant parts recorded a concentration of 56.345 ppm in the roots and 51.403ppm in the shoot.

The highest Cu concentration in soils at this site was the in soils of *Sphenoclea zeylancia* (2.217 ppm). Its shoot recorded a concentration of 0.801 ppm while the root recorded a concentration of 0.104 ppm. The recorded values are below the maximum allowable limit of the metal in soils which is 100 mg/kg.

Table 1: Identified plants at Eggon Community Mining Site

S/No.	Plant Name	Common Name	Location
1	*Eclipta alba*	False Daisy	EC_1 (0cm)
2	*Pseudognaphalium luteo*	Jersey Cudweed	EC_2 (0cm)
3	*Hyptis suaveolens*	Pignut	EC_3 (0cm)
4	*Physalis minima*	Native Gooseberry	EC_4 (50cm)
		Wild Cape Gooseberry	
5	*Cyperus rotundus*	Nut Grass	KS_5 (50cm)
		Nut Grass	EC_8(100cm)
6	*Sphenoclea zeylancia*	Goose weed	EC_6 (50cm)
7	*Acalypha indica*	Indian Acalypha	EC_7 (100cm)
		Three-Seeded Mercury	
8	*Calopogonium mucunoides*	Fact Sheet	EC_9 (100cm)

Key: EC = Eggon Community Mining site

Table 2: Concentrations of metals in plant parts at the mining site

Plant Name	Plant parts	Location	Ca (PPM)	Mg (PPM)	Mn (PPM)	Cu (PPM)	Pb (PPM)	P (PPM)
Eclipta alba	ROOT	NS1 (0Cm)	1.202	4.737	3.268	0.238	9.722*	5.62
	SHOOT	NS1 (0Cm)	20.177	8.122	5.734	3.203*	0.219	5.72
Pseudognaphalium luteo	ROOT	NS2 (0Cm)	29.566	7.655	0.949	0.460	14.692*	5.15
	SHOOT	NS2 (0Cm)	16.486	7.963	0.725	0.350	5.949*	5.48
Hyptis suaveolens	ROOT	NS3 (0Cm)	21.289	6.752	0.243	0.074	-0.228	4.20
	SHOOT	NS3 (0Cm)	11.804	7.730	1.428	0.265	0.641	5.30
Physalis minima	ROOT	NS4 (50Cm)	2.505	6.641	2.562	0.458	4.570*	4.80
	SHOOT	NS4 (50Cm)	34.778	8.099	2.237	0.411	6.996*	5.20
Cyperus rotundus	ROOT	NS5 (50Cm)	6.121	7.733	2.581	0.565	56.946*	5.77
	SHOOT	NS5 (50Cm)	1.788	5.881	1.432	0.272	28.439*	5.30
Sphenoclea zeylancia	ROOT	NS6 (50Cm)	7.224	8.482	6.292	0.104	56.345*	6.40
	SHOOT	NS6 (50Cm)	15.442	8.655	3.888	0.d801	51.403*	6.30
Acalypha indica	ROOT	NS7 100Cm)	2.088	7.819	0.929	0.592	6.111*	6.24
	SHOOT	NS7 100Cm)	13.382	8.043	4.711	0.549	14.00*	6.30
Cyperus rotundus (a)	ROOT	NS8 100Cm)	4.047	6.620	2.040	0.161	0.113	6.20
	SHOOT	NS8 100Cm)	5.506	7.231	1.231	0.204	0.470	6.10
Calopoganium mucunoides	ROOT	NS9 100Cm)	3.271	7.070	0.941	0.523	1.232	5.80
	SHOOT	NS9 100Cm)	61.511	10.031	9.715	0.407	0.671	5.60

Table 3: WHO permission limits for heavy metals in plants and soil

Element	Target Value of Soil (Mg/Kg)	Permission Value of Plant (Mg/Kg)
Cd	0.8	0.02
Zn	50	0.60
Cr	36	10
Cu	100	1.30
Pb	85	2
Ni	35	10

Target values are specified to indicate a desirable maximum level of elements in the polluted soils. Source: Dennman and Robbers 1990; Ministry of Housing, Netherlands 1994.

Table 4: Soil Analysis Result for the Mining Site

Parameter	Location	EC
Ca	0 cm	3.16 ± 0.14[b]
	50 cm	7.60 ± 0.70[c]
	100 cm	7.70 ± 0.81[d]
Mg	0 cm	1.60 ± 0.22[e]
	50 cm	5.06 ± 0.04[f]
	100 cm	5.13 ± 0.41[g]
Mn	0 cm	0.40 ± 0.10[a]
	50 cm	1.20 ± 0.19[a]
	100 cm	2.46 ± 0.93[a]
Cu	0 cm	0.18 ± 0.01[a]
	50 cm	1.40 ± 0.41[a]
	100 cm	0.65 ± 0.25[a]
Pb	0 cm	34.48 ± 17.33[a]
	50 cm	123.39 ± 57.38[a]
	100 cm	68.25 ± 35.53[a]
P	0 cm	3.63 ± 0.08[a]
	50 cm	3.73 ± 0.03[a]
	100 cm	3.53 ± 0.06[a]

BCF, TF AND EF of the Metals

The BCF of Pb was the highest in the *Pseudognaphalium luteo* (63.6 ppm) and the lowest BCF was recorded in *Hyptis suaveolens* (0.004) (Table 5). The highest BCF of Cu was also in *Pseudognaphalium luteo* (2.335) and its lowest BCF was in *Sphenoclea zeylancia* (0.048). Manganese on the other hand recorded highest BCF in *Sphenoclea zeylancia* (7.207) and the lowest recorded in *Cyperus rotundus* (0.215).

The TF for the heavy metals in the different plants found in this site revealed that for Pb, its highest TF was in the plant Ca*lopogonium mucunoides* (8.357) and the lowest TF recorded in *Hyptis suaveolens* (-2.811). Copper on the other hand recorded highest TF in *Sphenoclea zeylancia* (7.70), its lowest TF was recorded in *Cyperus rotundus* (0.481). For Manganese, the highest TF was recorded in Ca*lopogonium mucunoides* (10.324) and the lowest TF recorded in *Cyperus rotundus* (0.554).

The highest EF for Pb was recorded in *Pseudognaphalium luteo* (25.75) and the lowest EF was recorded in *Eclipta alba* (0.00). For Cu, its highest EF was recorded in *Pseudognaphalium luteo* (1.776) and the lowest EF was recorded in *Cyperus rotundus* (0.197). Manganese recorded its highest EF in *Eclipta alba* (9.248) and the lowest EF was recorded in *Cyperus rotundus* (1.077).

The plants that recorded EF less than one for Pb in this site include: *Eclipta alba, Hyptis suaveolens*, *Physalis minima, Cyperus rotundus, Sphenoclea zeylancia, Acalypha indica* and *Calopogonium mucunoides*. Also, plants with EF less than for Cu include: *Physalis minima, Cyperus rotundus, Sphenoclea zeylancia, Acalypha indica* and *Calopogonium mucunoides.*

Table 5: Bioconcentration Factor, Translocation Factor and Enrichment Factor of the metals at the mining site

Plant Species	Bioconcentration Factor (BCF)					Translocation Factor (TF)					Enrichment Factor (EF)				
	Pb	Cd	Cr	Cu	Mn	Pb	Cd	Cr	Cu	Mn	Pb	Cd	Cr	Cu	Mn
Eclipta alba	0.172	-	-	1.272	5.270	0.022	-	-	0.778	1.754	0.003	-	-	1.272	9.248
Pseudognaphalium luteo	63.6	-	-	2.335	3.476	2.445	-	-	1.693	0.763	25.75	-	-	1.776	2.655
Hyptissua veolens	0.004	-	-	0.430	0.759	2.811	-	-	3.581	5.876	0.0135	-	-	1.540	4.462
Physalis minima	0.044	-	-	0.638	1.741	0.404	-	-	1.314	0.873	0.0634	-	-	0.638	1.520
Cyperus rotundus	0.360	-	-	0.409	1.942	0.499	-	-	0.481	0.554	0.180	-	-	0.197	1.077
Sphenocleaze lancia	0.280	-	-	0.048	7.207	0.912	-	-	7.70	0.617	0.255	-	-	0.376	4.433
Acalypha indica	0.047	-	-	0.616	0.722	2.290	-	-	0.927	5.071	0.180	-	-	0.571	3.666
Cyperus rotundus[a]	4.159	-	-	1.267	0.215	0.017	-	-	1.15	5.071	0.074	-	-	1.457	1.092
Calopogonium mucunoides	0.544	-	-	0.778	0.523	8.357	-	-	3.902	10.324	0.0097	-	-	0.471	5.409

DISCUSSION

Sabo and Ladan (2004) recorded *Cyperus rotundus* at a Metalliferous mining site in Nahuta, Bauchi State Nigeria. This plant is a prevalent weed found growing in dismissed areas. It grows in all soil types and can survive an extreme temperature (Black *et al.,* 1965). The plant produces an extensive underground system from which they regenerate and become very difficult to control once established. The absence of Cd in the site could be attributed to the fact that calcium was recorded in high concentration and it is likely to suppress the concentrations of Cadmium. This is in line with the report of Naoko *et al.* (2011), where they reported that the transport of Cd from the roots through stems and leaves are suppressed by Calcium treatment, indicating that the presence of Ca regulates Cd transport from the roots. Franziska (2016) also reported that Ca and the toxic heavy metal Cd are antagonistic ions competing for uptake in plants when they co-occur in soil solutions and high calcium concentrations can reduce the uptake of Cd in plants.

Chromium on the other hand, was also not recorded in any of the plant parts. Cr is a toxic non-essential element to plants; hence they do not possess specific mechanism for its uptake. Therefore, the uptake of this heavy metal is through carriers used for the uptake of essential metals for plant metabolism. The pathway of Cr (VI) transport is an active mechanism involving carriers of essential anions such as sulfate (Cervantes *et al.,* 2001). Iron, Sulphur and Phosphorus are known also to complete with Cr for carriers building (Wallace *et al.,* 1976). Adequate concentration of phosphorus was recorded in the site. This could likely be the reason why the presence of Chromium was hindered. This evidence was provided by Bolan *et al.,* 2003 where they reported that phosphorus compounds both the water soluble and the water insoluble (e.g. apatite also known as PRs). Phosphorus compounds are known to immobilize metals in soils hereby reducing their bioavailability for plant uptake. They also mentioned that even though mobilization by some of the phosphorus compounds enhances the bioavailability of metals, immobilization inhibits their plant uptake and reduces their transport in soils and subsequent ground water contamination.

Magnesium is also said to have inhibitory properties against Cadmium. Over the last decade, studies have revealed the ability of Mg^{2+} to mitigate heavy metal toxicity caused by aluminum (Al^{3+}) and Cadmium (Cd^{2+}) (Base *et al.,* 2011; Kashen and Kawai, 2007). Kashen and Kawai (2007) reported that adding Mg^{2+} to nutrient solutions reduced Cd concentration in plants and enhanced the growth of plants suffering from Cd toxicity. Hemans *et al*. (2011) indicated that the protective effect of Mg^{2+} against Cd toxicity may be at least partly attributed to the protection of the photosynthetic apparatus.

Manganese was recorded but not at a high concentration, this could be attributed to the fact that both calcium and Magnesium were recorded in high concentrations and they are likely to suppress the concentration of Manganese. This corresponds with the report by Nazrul-Islam (1985) where he investigated the effect of calcium and manganese interaction on the growth and nutrition of *Epilobium hursutum* L. The author discovered that increasing calcium level in the nutrient solution was effective in reducing manganese toxicity. The uptake of manganese in the root decreased with increasing calcium level in the nutrient solution while in the shoots iron content decreased and the accumulation of mg also decreased both in root and shoot with the increase of the manganese level in the nutrient solution. Eugene *et al.,* (1968) also studied the mutual effects between Mn, Ca and Mg during steady-state adsorption experiments with excised barley roots. Calcium appeared to enhance the role of Mn absorption whereas Mg had a highly depressive effect. The combination of both Mg and Ca was even inhibitorier to Mn absorption than Mg alone.

The recorded concentration of copper is lower than that reported by previous studies (Ogundele *et al.,* 2015; Sabo & Ladan, 2014).

The plant *Eclipta alba* is an invasive species that is much-branched, variable, prostrate ascending, or erect. It is a rough hairy annual herb. *Cyperus rotundus* is capable of growing in almost every soil type over a wide range of soil pH (Holm et al., 1977). Lead is absorbed by plants mainly through the roots from soil solution. After the uptake of Lead by plants, it primarily accumulates in root cells because of the blockage by casparian strips within the endodermis. Its uptake leads to impaired uptake of essential elements such as Mg and Fe.

These differences in the concentrations of Calcium and Magnesium recorded indicate that distance plays a role in the concentration of metals in soil at the mining site. Cadmium and chromium was also not detected in any of the soil samples and it could be attributed to the fact that some of the minerals in the soil were inhibitory to the presence of cadmium and chromium just as seen with the plants. The high concentration of Pb in the site could be as a result of the site being a predominant source of this metal (i.e Galena Mining site). The recorded concentration of Pb exceeds those reported by the previous authors (Sabo and Ladan,2014). The concentration of Cu also exceeds that reported in the previous Mining site and Idzi *et al*. (2012). But it is below the recorded concentration by Sabo and Ladan (2014).

At the mining site, *Pseudognaphalium luteo* could be described as a phytoextractor while *Cyperus rotundus* as a phytostabilizer of Pb. Also, *Pseudognaphalium luteo* and *Cyperus rotundus* as phytoextractors whereas *Eclipta alba* as phytostabilizer of Cu. *Eclipta alba* is a phytoextractor while *Pseudognaphalium luteo, Physalis minima, Cyperus rotundus* and *Sphenoclea zeylancia* are phytostabilizers of Mn. As earlier stated, plants that are able to extract metals from soil and store them in their above ground parts have Enrichment Factor (EF) greater than one which emphasizes on the extent of metal uptake by plants.

CONCLUSION

The research revealed that indigenous herbaceous plant species could be used to remediate heavy metals impacted soil due to Mining activities at Eggon Community Mining sites. These plant species could also be used to restore the degraded vegetation in these sites. Even though none of the plants could act as hyperaccumulator, a significant amount of them were able to act as phytostablizers and phytoextractors for the investigated metals. The Mining site showed a higher concentration of Pb in exploitable quantities due to ongoing Galena Ore mining at the site. Plant nutrients tend to ameliorate heavy metal toxicity as it has been seen with Ca and Mg, reducing toxicity of manganese while phosphorus reducing lead toxicity. The level of metals that lied within the normal range for plants may become significantly high with time and continual consumption of the plant growing around these locations could result in their accumulation in the body of their consumers thereby position health risk in future, though a more rigorous approach is however needed to understand the mechanism of absorption of these metals by plants.

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