Bioaccumulation of Heavy Metals in Mechanic Workshops

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Abstract: **Mechanic workshops are one of the major reasons for the environmental influx of heavy metals in the environment. The accumulation and partitioning of Cadmium, Chromium, Copper, Lead, Zinc and Manganese in *Azadirachta indica* plants growing on two mechanic workshops (Dass park and Mechanic village) and one control site (farm land) within Bauchi Metropolis were therefore studied, using the Atomic Absorption Spectrophotometer, in order to find out their phytoaccumulation potentials. The weighted mean of the metals in the *Azadirachta indica* plants growing on Dass Park was as follows: Cu(86.87mg/kg)>Zn(63.18mg/kg)>Mn (57.33mg/kg)>(Pb17.04mg/kg)>Cr(7.55mg/kg)>Cd (2.71mg/kg), while in Mechanic Village, the order was: Cu (63.78mg/kg)>Zn(63.44mg/kg)>Pb (31.45mg/kg) >Mn(31.37mg/kg)>Cr(8.05mg/kg) >Cd (1.80mg/kg). The weighted means of the various metals under investigation in the mechanic workshops were higher than those obtained in the control site, but were all within the normal range in soils, except for Cd. ANOVA results showed that significant differences in the metals studied existed among some of the aerial parts of the studied plant. The average concentration factors of *Azadirachta indica* in the six elements studied at both contaminated sites were in the order: Cu (0.94)>Zn (0.34)>Mn (0.25) >Pb (0.15)>Cr (0.13)> Cd (0.12). The accumulation ability of *Azadirachta indica* for metals except Cd and Cr were observed to be moderate and high for Cu.**

Keywords: **Phytoremediation, *Azadirachta indica*, Heavy Metals, Pollution.**

I. INTRODUCTION

The term “heavy metal” is commonly adopted as group name for the metals and metalliods, which are associated with pollution and toxicity but also, include such metals which are essential for living things at low concentrations [1]. Heavy metals are a class of trace metals with density greater than $5.0gcm^{-3}$ [2], [3]. Trace metals are the main sources of toxicity problem in the environment due to their persistent nature [4], [5], [6], [7], [8],[9]. All trace elements are toxic to living organisms at excessive concentration but some are essential for normal healthy growth and reproduction by plants and animals at low but critical concentrations. Deficiencies in these essential elements or micronutrients can lead to disease or even death of the plant or animals [10], [11].

The increase in heavy metal pollution of soils within and around mechanic villages would result in their increase in water bodies (surface and underground) within and away from the vicinity of the mechanic village due to the continuous interaction between soil and water [12]. Automobile mechanic activities have been widely reported as one of the major sources of heavy metal pollution of the ecosystem in Nigeria [13], [14], [15]. Wastes from these workshops are being discharged at random on soils, polluting productive soils, natural water system as well as ground water. These wastes contain heavy metals such as Cd, Cr, Pb, and Fe, Ni, Zn, Co, Cd, Cu, Ba [16], [17], [3].

The remediation of these soils therefore posses a lot of difficulties to individuals and government agencies. According to [18], the US phytoremediation market was expected to expand more than ten-fold between 1998 and 2005, to over $214 million. Contaminated soils therefore represent an economic liability as well as a technical challenge.

The remediation of these soils could be carried out by physical removal of the contaminated soils, followed by treatment technologies such as soil washing, solidification and stabilization, chemical treatment, vitrification, thermal desorption, electro kinetics and incineration but that these cleanup methods are expensive and render the land useless as a medium for plant growth, remove all biological activities including useful microbes, such as nitrogen fixing bacteria and mycorrhizal fungi, as fauna [19], [20], [21], [22]. Hence the need for plants, especially large one in phytoextraction studies, since the burden of harvesting and disposing one season plants poses greater difficulties in applying phytoremediation [23].

Several small plants have been reported for their phytoremediation abilities. These include *Brassica Junicea* (for Pb), *Lycopercium esculentum* (for Pb and Zn), Alpine pennycress (for Cd and Zn), *Helianthus annuus* (for As and Pb), Zea mays (for As, Cr and Cu), *Piptatherum miliaceum* (for Pb) [24], [25], [26], [27], [22], [28].

However, researchers are finding out that trees (rather than smaller plants) potentially the lowest-cost plant type to use for phytoremediation and that the use of trees allows them to treat deeper contamination because tree roots penetrate more deeply into the ground [29], [30], [31]. The common mulberry tree (*M. rubra***)** has been shown to release chemicals, that support the growth of bacteria that break down PCBs, and willow trees absorb cadmium, zinc, and copper [32]. Native naturally colonizing plant species may be used for the bioremediation of Fe tailings, as they stabilize and reduce soil erosion [33].

While data exist on the in-situ and ex-situ phytoextraction of heavy metal by some large plants growing on minning areas [34], on sugar mill effluent polluted soil [35] and on tannery polluted soil [36], [23]. Nothing exists in the phytoaccumulation of heavy metals by these plants in studies carried out on plants in Nigeria, especially with respect to automobile repairs or mechanic workshops.

The aim of this research is to therefore investigate the ability of *Azadirachta indica*, growing on automobile sites, to accumulate cadmium, chromium, copper, lead, manganese and zinc.

II. MATERIALS AND METHODS

A. Study area

The study was carried out in two automobile repair and maintenance sites (Dass Park and Mechanic village) and one control site within Bauchi metropolis, Bauchi local government area of Bauchi state. Dass Park is located along Dass road while Mechanic village is situated along Jos road. Geographically, Bauchi state lies between latitudes 9^0 30 N and 12^0 34' and longitude 8^0 5' E and 11^0 00' E of the Greenwich meridian. It occupies a total area of 549,259.01 sq. kilometers representing about 5.3% of the land mass of Nigeria. The state spans two vegetation zones namely Sudan and Sahel Savanah. Effective rains start in mid may or sometimes around early June and ends in late October. The dry season starts in October and ends in May. The average annual rainfall is between 1000mm and 1300mm.

B. Soil sample collection and preparation

Soil samples were collected from ten (10) different points on each of the two (2) study areas at soil depth of 0 – 30cm and stored in polyethene bags. All the samples were collected immediately between August and September, 2010. The soil samples from each of the study sites were thoroughly mixed together, conned and quartered several times before the required samples (500g) for analysis were obtained. The samples were then air dried, crushed in a mortar and sieved through a 2mm sieve [27].

C. Laboratory determinations

The ground dried plant samples were digested with a mixture of conc. HNO_3 and 70% $HClO_4$ in the ratio of 3:1.ater [37]. Each sample extract were then placed in plastic bottles. The air-dried, ground and sieved sample were accurately weighed and digested in a 1:1 mixture of concentrated nitric acid perchloric acid [27], [28]. The digested samples were then subjected to analysis of the six metals using the Atomic Absorption Spectrophotometer (A Analyst 400, Perkin Elmer, U.S.A).

D. Plant samples collection and preparation

The leaves, barks and roots were collected from three randomly selected *Azadirachta indica* plants in the mechanic workshops and stored in paper bags. Root tissues were sampled from what was considered to be the surface roots of these plants. The plant samples were washed thoroughly, cut into smaller pieces and oven- dried at 60^oC for three (3) days. The dried samples was ground to powder and stored in labelled polythene bags [28], [38].

III. RESULTS AND DISCUSSION

The heavy metal contents of *Azadirachta indica* plants tissues and the weighted mean concentration in the various study sites are shown in Table I. Table II captions the average translocation ratio (TR) and concentration factor (CF) of detected metals in the plant. The transfer ratios of the heavy metals from the root to the leaves and the bark are given in Table III.

A. Accumulation of metals in Azardirachta indica on the contaminated sites

The result in Table I shows that the weighted means of the metals in the whole plant in Dass Park (DP) is in the order: Cu (86.87mg/kg)> Zn (63.18mg/kg)>Mn (57.33mg/kg)>Pb (17.04mg/kg)>Cr (7.55mg/kg)>Cd (2.71 mg/kg). In the Mechanic Village (MV), the weighted mean is in the order: Cu (63.77mg/kg)>Zn (63.47mg/kg)> Pb (31.46mg/kg) >Mn (31.37mg/kg)>Cr (8.05mg/kg)>Cd (1.80mg/kg). Except for Cd (in DP) and Pb (in MV), the mean metals accumulation in this trees growing on the sites were within the range of the metals in plants. The observed trend of accumulation of the metals in this tree in the M.V was different from that of the DP, although the concentrations of Cd, Cr and Zn are almost similar in both automobile sites. In both sites, a decreasing trend was observed from Cd to Cu (Fig. 1).

TABLE I: ACCUMULATION OF AVERAGE HEAVY METALS (PPM) IN *AZADIRACHTA INDICA*

Metal	DASS PARK				MECHANIC VILLAGE				CONTROL SITE				Normal Range In Plants
	Leave	Bark	Root	Weighted mean	Leave	Bark	Root	weighted mean	Leave	Bark	Root	weighted mean	
Cd	7.87^{a}	0.15^{b}	0.10^{b}		5.05^{a}	0.20^{b}	0.15^{b}		ND	ND	0.15		ж **0.1-2.4**
	±1.12	±0.87	±0.10	**2.71**	±0.58	±0.13	±0.04	**1.80**			±0.50	**0.05**	
Cr	1.98^{a}	15.43^{b}	5.25^{c}		3.68^{a}	13.96^{b}	6.50^{c}		ND	1.30	0.43		жж**0.03-14**
	±0.02	±1.02	±0.05	**7.55**	±0.45	±0.57	±0.50	**8.05**		±0.04	±2.83	**0.58**	
Cu	31.65^{a}	101.30^{b}	127.60^{c}		30.05	72.65^{b}	88.55^{b}		14.30	20.20	31.85		жж **5 - 20**
	±4.05	±20.50	±11.20	**86.87**	±2.60	±9.50	±5.40	**63.78**	±2.11	±3.05	±4.65	**22.11**	
Pb	16.43^{a}	19.13^{b}	15.57^{a}		15.67^{a}	62.80^{b}	15.90^{a}		7.367	12.87	9.05		жж**0.2-20**
	±1.44	±3.86	±1.46	**17.04**	±1.29	±3.27	±0.82	**31.45**	±1.01	±0.40	±0.79	**9.74**	
Mn	51.43^{a}	76.53^{b}	49.03^{ac}		35.73^{a}	26.77^{b}	31.60^{a}		21.23	23.87	15.72		ж**20-1000**
	±4.29	±16.80	±2.38	**57.33**	±1.37	±3.67	±4.81	**31.37**	±6.41	±3.20	±0.39	**20.27**	
Zn	53.63^{a}	66.73^{a}	69.17^{b}		61.10^{a}	68.70^{a}	60.53^{a}		20.40	25.95	20.69		жж **1-400**
	±6.03	±7.92	±8.04	**63.18**	±5.15	±4.19	±9.02	**63.44**	±1.15	±3.08	±1.13	**22.35**	

ж Alloway,1996, ж ж Oyelola et al., 2009, ND – Not detected, Values within a row with different superscripts are significantly different ($p < 0.05$).

In both contaminated sites, it was observed that the order of metal concentration showed that $Cd_{leave} >> Cd_{bark} = Cd_{root}$, while $Cr_{bark} > Cr_{root} > Cr_{leave}$. In DP, $Cu_{root} > Cu_{bark} > Cu_{leave}$ while in MV, $Cu_{root} = Cu_{bark} > Cu_{leave}$. No significant difference was observed in the accumulation pattern of Pb in the various parts of the plant in D.P, while in M.V, the order obtained was $Pb_{bark} > Pb_{leave} = Pb_{root}$. Mn in the leaves and roots in both sites were not significantly different. It was observed that for Zn, no significant difference was observed among the tree parts in the MV. [38] reported a similar pattern for Zn accumulation in *Rhizophora mucronata* (spp).

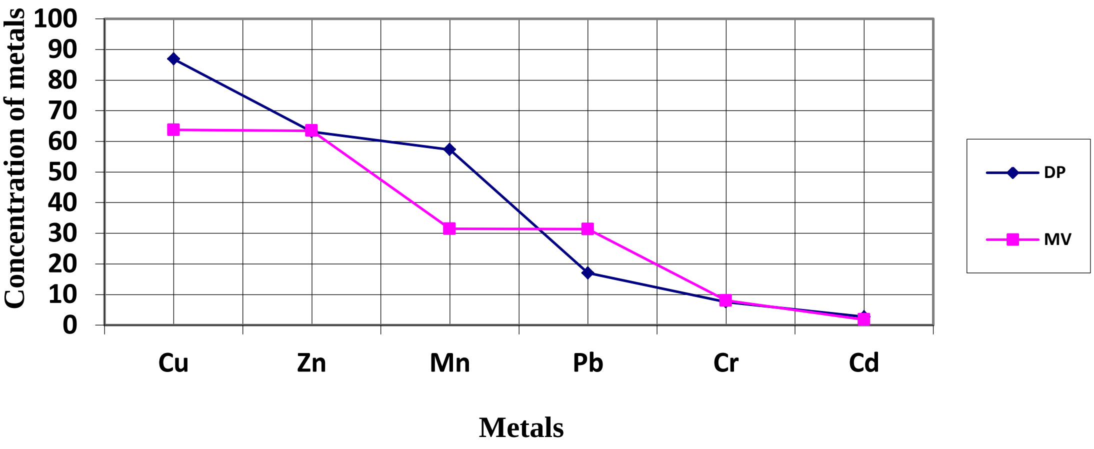

Fig. 1 Accumulation trends of the Metals in *Azadirachta indica* on the Automobile Sites

Fig. 2 and 3 show the percentage accumulation of the metals in each part of *Azadirachta indica* from the study sites. In both contaminated sites, it was observed that more than 90% of the Cd in the plant accumulated in the leaves than the other parts of the plant. The accumulation of Cd in this part of the plant may be due to atmospheric deposition of the metal from non-ferrous metal activities, fossil atmospheric deposition of the metal from non-ferrous metal activities, fossil combustion e.t.c; The accumulation of Pb in the leaves of this plant was high (32.13% in D.P). This may be due to foliar uptake. 90-99% of Pb obtained in the leave materials is due to foliar uptake while the high percentage of this metal in the bark of the plant may be as a result of the fact that the uptake of Pb by plant roots and translocation to the shoot vary seasonally.

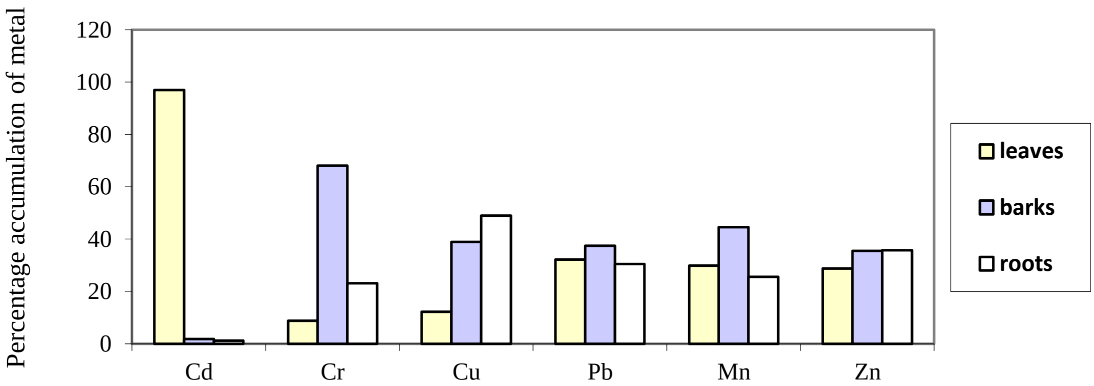

Fig. 2 Percentage accumulation of metals by each plant component of *Azadirachta indica* in Dass Park

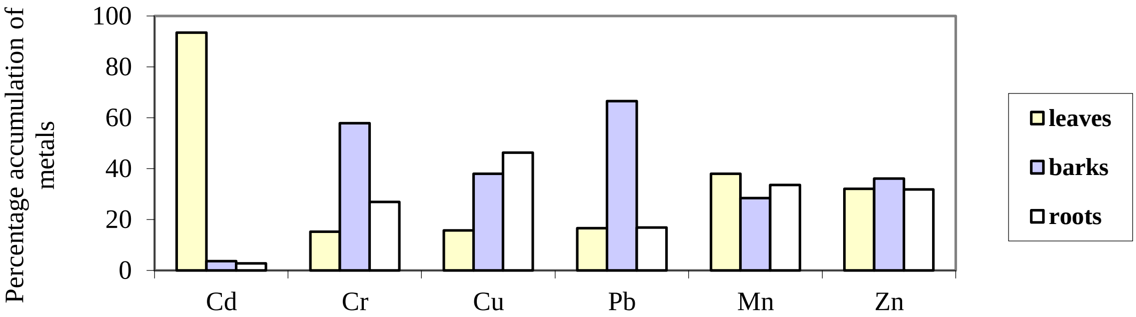

Fig. 3 Percentage accumulations of metals by each Component of *Azadirachta indica* in Mechanic village

enerally, the level of Pb in this plant (in MV) was high. The excess of Pb in this site (MV) could be attributed to lead from car exhaust fumes, derived from leaded fuel, abraided tyre materials and car batteries, which are higher on this site, when compared to DP. The high zinc concentration is explainable, since Zn is an essential trace element for humans, animals and higher plants [1], [38]. The high concentration of Cu in this tree in both automobile sites is also explainable, since Cu is used in the production of wire and alloys used in automobiles [40].

B. Translocation of heavy metals in Azadirachta indica

Translocation ratio (TR) of metal is the ratio of the concentration of heavy metal in the aerial parts of a plant to the concentration of the heavy metal in the root $[HM]_{aerial}/[HM]_{root}$. Translocation ratio gives a picture of the mobility of metals from the aerial parts of the plant [38].

The mean calculated translocation ratio in the leaves was in the order: Cd>Mn>Pb>Zn>Cr>Cu (Table 2). The high translocation ratio (TR) for Cd is significantly different from the others in the leaves, with Cd, Pb and Mn exceeding a translocation ratio of 1. The high TR for Cd, Mn and Zn may be due to the fact that they are readily translocated to the top after absorption [1].

TABLE II: AVERAGE TRANSLOCATION RATIO (TR) AND CONCENTRATION FACTOR (CF) OF METALS TO LEAVES AND BARKS AND AZADIRACHTA *INDICA* IN THE STUDY SITES

Metals		Cd	Cr	Cu	Pb	Mn	Zn
Average Translocation Ratio (TR)	**Leaves**	56.17 ±31.8	0.47 ±0.13	0.29 ±0.06	1.02 ±0.05	1.15 ±0.03	0.91 ±0.15
	Bark	1.42 ±0.12	2.54 ±0.56	0.81 ±0.11	2.59 ±1.92	1.29 ±0.63	1.16 ±0.23
Average Concentration Factor (CF)		0.12 $\pm0.09^a$	0.13 $\pm0.16^a$	0.94 $\pm0.34^b$	0.15 $\pm0.07^a$	0.25 $\pm0.11^a$	0.15 $\pm0.07^a$

(Values within a row with different superscripts are significantly different ($p< 0.05$)).

In the case of the bark, the metal translocation ratio (TR) was as follows, Cu<Zn<Mn<Cd<Cr<Pb. It has been observed that the TR of Cu to the shoot is low, compared to the other metals, showing that plants have the capacity to be extremely tolerant of such metal, with preferential accumulation mainly in the root tissue [38]. This explains the low TR for Cu in this plant.

C. Ability of Azadirachta indica to absorb metal in the contaminated sites

The concentration factor (CF), which is the ratio of metal in the plant to the concentration of metal in the soil.(ie C.F= $[HM]_{Plant}$ (mg/kg)/ $[HM]_{Soil}$(mg/kg)), gives an idea of the ability of a plant to accumulate metals absorbed from the soil and reveals the accumulation pattern in the plants. In addition, CF quantifies the relative differences in the bioavailability of metals to plants [38].

From table II, the average concentration factors (CF) of *Azadirachta indica* in the six elements studied at both contaminated sites were in the order: Cu> Zn> Mn> Pb> Cr> Cd. The CFs of the metals were lower than 0.50, except for Cu (with CF 0.944±0.34). The average CF value obtained for Cd in the present study was lower than those reported by [34]. For Cu, Pb and Zn, the average CF values in this study were higher than those reported by [34]. This result shows that the accumulation ability of *Azadirachta indica* for metals except Cd (CF= 0.12) and Cr (CF= 0.13) is moderate and high for Cu(CF= 0.99). This result shows that the accumulation ability of *Azadirachta indica* for metals except Cd (CF= 0.12) and Cr (CF= 0.13) is moderate and high for Cu (CF= 0.99).

D. Heavy metal enrichment in the study sites.

The heavy metal concentrations in the two mechanic workshops were well over those of the control site (Table III). [12] reported a similar result, indicating that the metals concentrations in three mechanic villages in Imo state were well above the local background values. Although the metal enrichment in this present study was lower than those reported by [12], except for Cd and Cr. The present results obtained for Cd, Cr, and Pb are similar to those reported by [40] in automobile workshops in Akure.

Table III: Heavy Metal Enrichment (ppm) of Soils in the Automobile contaminated sites and Control site

Metal	Cd	Cr	Cu	Pb	Mn	Zn
Dass Park	16.90 ^{a}	62.03^{a}	73.60^{a}	168.6^{a}	177.50^{a}	197.40^{a}
	±3.35	±2.63	±11.30	±3.27	±2.29	±2.29
Mechanic Village	31.35^{b}	55.50^{a}	90.20^{b}	160.30^{a}	184.41^{a}	175.72^{a}
	±5.33	±5.47	±9.25	±10.50	±12.00	±14.60
Control site	1.52	9.47	24.35	37.57	44.77	72.70
	±0.57	±0.83	±3.60	±3.89	±9.42	±13.60
Normal range in soil	0.01-2*	5-1500 **	2-250 **	2-300 **	20-10,000*	1-900 **

(* Alloway,1996, **Oyelola et al., 2009), Values within a column with different superscripts are significantly different ($p < 0.05$).

The order of abundance of the metals in Dass park (D.P) and Control site (C.S) were Zn>Mn>Pb>Cu>Cr>Cd while in the Mechanic village (M.V), the order was Mn>Zn>Pb>Cu>Cd>Cr. The order in the M.V was similar to results obtained by [3] in Akure and in Nekede M.V [12].

The values obtained in the contaminated and control sites in this study are within the normal range in soils except for Cd (Table III). The enrichment of Cd and Cu in both automobile sites were significantly different, while Cr, Pb, Mn and Zn were not. The accumulation of Cd and Cu were higher in the Mechanic Village.

E. Pearson Bivariate Correlation Coefficient for Metals in Azadirachta indica (Whole Plant)

A highly significant positive relationship was observed between the levels of Cu and Pb ($r=0.938$; $p< 0.01$) and between the levels of Mn and Zn ($r=0.95$; $p< 0.01$), as shown in Table 4. This indicates that an increase in the concentration of Cu would result in an increase in that of Pb while the increase in Mn concentration would lead to increase in the concentration of Zn.

TABLE IV: PEARSON BIVARIATE CORRELATION COEFFICIENT FOR METALS IN *AZADIRACHTA INDICA* (WHOLE PLANT)

		Cd	Cr	Cu	Pb	Mn	Zn
Cd	**R**	1					
	P						
Cr	**R**	.762	1				
	P	.078					
Cu	**R**	.704	.793	1			
	P	.119	.060				
Pb	**R**	.720	.682	.938(**)	1		
	P	.106	.136	.006			
Mn	**R**	.643	.366	.482	.604	1	
	P	.168	.476	.333	.204		
Zn	**R**	.794	.577	.633	.755	.954(**)	1
	P	.059	.230	.177	.082	.003	

** Correlation is significant at the 0.01 level.

IV. CONCLUSION

The concentration factors for Cu, Pb and Zn in *Azadirachta indica* in this study for all the metals in this study range from moderate to high, except for Cd and Cr. Phytoextraction can therefore be used to reduce the migration of contaminants in soils and underground water. The heavy metal concentrations in the two mechanic workshops were within the normal range in soils, except Cd and Cr. The reduced levels of some of the metals in this study, when compared to the other works may be as a result of the presence of tree and other plants growing on the study sites.

Deliberate efforts should therefore be made to ensure that local trees with phytoaccumulation potentials are planted in and around mechanic villages to serve as trap for these heavy metals and help to reduce the migration of contaminants in soils and underground water.

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