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Determination of Heavy Metals in Sawdust Particles, Distribution in Soil and Accumulation in Plants at Ahiaeke Timber Market in Umuahia, Nigeria

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ABSTRACT

Farmers are constrained to farming on lands adjoined to sources of pollution without considering the health implications of consuming crops grown on such lands. The main route of entry of heavy metals in human body is via ingestion of food contaminated with heavy metals. Heavy metal toxicity has proven to be a major threat and there are several health risks associated with it. This, therefore, necessitated the determination of heavy metals in sawdust, distribution in soil and accumulation in plants at Ahiaeke timber market in Umuahia, Abia State. The study assessed metals (chromium [Cr], zinc [Zn], cadmium [Cd], and copper [Cu]) in sawdust particles, their distribution in soil and accumulation in plants. The highest concentration of Zn $(51.00\pm1.84 \text{ mg/kg})$ and Cr $(0.170\pm0.014 \text{ mg/kg})$ was observed at the sawdust dump 2, Cu $(8.24\pm0.60 \text{ mg/kg})$ was highest at sawdust dump 1 while Cd (4.72±0.071 mg/kg) was highest at sawdust dump 3. The values of the highest concentration of Zn (119.7 \pm 7.02 mg/kg), Cu (75.85 \pm 4.80 mg/kg) and Cd (22.39±3.30 mg/kg) in soil were observed in 0-10 cm depth at the distance of 20 m. The values of Zn (119.7 \pm 7.02 mg/kg) and Cd (22.39 \pm 3.30 mg/kg) in soil is above the maximum permitted levels of 60 mg/kg (Zn) and 0.1 mg/kg (Cd) established by the Codex Alimentarius Commission. The highest concentration of Zn (34.70 \pm 7.05 mg/kg), Cu (5.34 \pm 0.11 mg/kg) and Cd (2.94 \pm 0.515) in plants was assimilated by Centrosema pubescence. The level of Cd in plants is well above the permissible limit (PL) 0.3 mg/kg set by FAO/WHO for vegetables and herbs. Consumption of such contaminated C. pubescence can be a route of entry of Cd in grazing animals' vis-à-vis the people who depend on such herbivores for protein.

Keywords: Sawdust, Heavy metals, Soil, Plants, Distance, Depths

1.0. Introduction

The environment is continuously being contaminated by various human activities, such as industrial production, agricultural processes, and mineral exploitation, food processing, commercial, social, and domestic activities that generate contaminants like heavy metals. The release of heavy metal is of great concern all over the world since metal are non-biodegradable (Wu and Zhang, 2010) and cannot be detoxified and removed by metabolic activities once they are available in the environment. This can result to the building-up of toxic levels in terrestrial and aquatic ecosystem. Metals such as zinc (Zn), copper (Cu), manganese (Mn), iron (Fe), and nickel (Ni) are required by living organism to support their metabolic function but are toxic when they exceed their normal threshold in soil through external addition. Non-essential metals such as lead (Pb), chromium (Cr), mercury (Hg) and cadmium (Cd) are not needed for growth of living organisms (Kabata-Pendias, 2011).

Plants growing on metal contaminated soil tend to absorb metals from soil solution via the roots and translocate it to the stems and the leaves. Their (metals) chemical form in soil can strongly influence their uptake by plants (Pitchell and Anderson, 1997) through the roots (either as mobile ions present in the soil solution) (Davies, 1983) or through foliar absorption (Chapel, 1986) resulting in

bioaccumulation of the elements in plants tissues (Amusan *et al.*, 2005). This however, is dependent on the type of metal, plant species and plant part (Juste and Mench, 1992). The exploitation of such trees at maturity and subsequent processing at timber markets will result to release of metal in form of dust particles in the environment. The increasing demand for wood as building material, for furniture purposes, sculptural work, and in various industries vis-à-vis poor planning and ineffective implementation of budget allocation for waste collection and disposal by the Government has resulted to high volumes of sawdust waste at dumpsites in Umuahia timber market. The decomposition of the sawdust may culminate to contamination of the immediate surroundings via leaching of metals and other chemical pollutants into the soil. The concomitant effect is possible ecological imbalance and deterioration in the quality of plant products around the vicinity. Similarly, it may result to bioaccumulation of metals in plants; hence culminate to bio magnification in food chain via herbivorous animals and man that depend on such plants for food and medicine.

Heavy metal toxicity has proven to be a major threat and there are several health risks associated with it (Mathew *et al.*, 2014) which include hyperkeratosis, loss of skin pigmentation, cancers of the skin, bladder, and lung (WHO, 2001), vomiting, diarrhea, abdominal cramps, liver and kidney damage (Plunkett, 1987), impair reproduction and abnormal development of children, nervous and immune systems, dental and skeletal fluorosis (Finkelman, 2007). Quite a number of studies on sawmilling and/or wood processing activities have been carried out in terms of the health effects of workers of the sawmills (Boateng and Amedofu, 2004; Ugheoke *et al*, 2006; Oke and Oyedare, 2006; Arimoro *et al*, 2007; Verma *et al*, 2007; Lasode and Balogun, 2010; Bello and Mijinyawa, 2010; Edith and Nkwocha, 2012), heavy metals in sawdust particles (Nwajei and Iwegbue, 2007; Ncube and Phiri, 2015) and soil (Ezekiel *et al.*, 2013). Literature search show that no work has been done on metal accumulation in plants at timber market or sawmills. This study, therefore, attempted to fill this gap by investigating heavy metal distribution in soil and accumulation in plants at Ahiaeke timber market, Nigeria. The specific objectives were to identify some metals in sawdust, their distribution in soil at various depths and distances and accumulation in plant species around the timber market sawdust dumpsite.

2.0. Methodology

2.1. Description of study area

The study was carried out at the Ahiaeke timber market located at Ahiaeke in Umuahia North, Abia State, Nigeria. Ahiaeke lies on latitude 05° 29' to 05° 42' N and longitude 07° 24' to 07° 33'E, and it is located on the low land rainforest zone of Nigeria (Keay, 1959). The area has two distinct seasons in a year which are the wet season and the dry season. The rainy season covers a period of seven months from April to October, while dry season last for four months from November to March each year with an average rainfall of 2238 mm per year (Ogbonna and Nzegbule, 2009). Its minimum and maximum temperature is 23 and 32 °C, respectively and a relative humidity of 60-80 % (Ogbonna and Nzegbule, 2009) while the estimated terrain elevation above sea level is 155 m. Agriculture is the major occupation of the people where over 70 % of the population engages in subsistent farming and the main food crops grown are yam, maize, cassava, cocoyam, banana, plantain, palm tree and raffia palm.

2.2. Sawdust analysis of the timber market

A reconnaissance survey was carried out prior to sample collection at the timber market. This was to identify the location of the sawdust waste dumps and plant species commonly found at the site. Three sawdust waste dumps (1, 2, and 3) were located at the Ahiaeke timber market. Sawdust particles were collected randomly from fifteen different sampling points in four cardinal points (i.e. three sampling points each at north (N), south (S), east (E), west (W), and at the centre (C) of the dumps from each dump. Samples from each particular sawdust dumps (e.g. 15 sampling points at N, S, E, W, and C dumpsite 1) were placed (about 2 kg) in large, well cleaned cellophane bags (of Abia State Environmental Protection Agency (ASEPA) and transferred to the laboratory for pre-treatment and analysis. The sawdust was sieved through 0.2 mm sieve, and sawdust that passed through the sieve was kept in a refrigerator prior to digestion. A 2 g of the sieved sawdust was weighed and digested in acid mixture prepared from 15 ml nitric acid and 3 ml perchloric acid. The solutions were kept on a

hot plate at 130 °C for 2 hrs. The clear digest was slowly evaporated and on cooling, the solution was filtered and the filtrate was diluted to 25 ml using deionized water. The concentrations of chromium (Cr), zinc (Zn), cadmium (Cd), and copper (Cu) in the digested samples were determined using flame Atomic Absorption Spectrophotometer, AAS (PG Instrument, model: Pg-500, UK)) after calibrating the equipment with different standard concentrations.

2.3. Soil analysis of the experimental site

Soil samples were collected randomly from eight different sampling points at 0-10, 11-20, and 21-30 cm soil depth with well cleaned Dutch soil auger in four cardinal points (i.e. two sampling points each at north (N), south (S), east (E) and west (W) of 20, 40, 60 and 80 m from the centre of the sawdust wastes dumps. The control sample was collected in a 5 year upland bush fallow about 500 m from the dump sites where there was no visible source of contamination. Samples from each particular soil depth (e.g., 0-10 cm at N, S, E and W) were placed in cellophane bags (about 20 g), labelled well, and were transferred to the laboratory for pre-treatment and analysis. Samples from the same soil depth were bulked together to give composite samples which were homogenized and air-dried in a circulating air in the oven at 30 °C to a constant weight and passed through a 2 mm sieve. Subsamples from the composite samples were then digested. About 10 ml of nitric acid was added to 2 g of air dried and processed soil in a 100 ml beaker and the mixture was reacted and heated by the addition of 3 ml of perchloric acid, allowed to stand for 15 min. The mixture was digested by heating gently at low temperature on a hot plate and allowed to cool for 5 minutes. The digest was then filtered with Whatman No. 41 filter paper into 50 ml standard flask. The suspension was filtered into 50 ml standard flask and diluted with de-ionized water to 100 ml mark. The concentrations of chromium (Cr), zinc (Zn), cadmium (Cd), and copper (Cu) in the digested samples were determined using flame Atomic Absorption Spectrophotometer, AAS (PG Instrument, model: Pg-500, UK)) after calibrating the equipment with different standard concentrations. The calibration curves were prepared from standards by dissolving appropriate amounts of the metal salts in purified nitric acid, diluting with deionized water and storing as stock solutions in a quartz flask.

2.4. Plant sampling and analysis of metals

In this study, plant sampling for determination of heavy metals content in plants was carried out on individual plant species that had up to five (5) number of occurrence in each of the distances (20, 40, 60 and 80 m) at the sawdust waste dumpsite and control site. Fresh leaves were sampled from different shoots and parts of different plant species 4-5 years of age. The leaves of *Eleusine indica* L. (goose grass, Family-Poaceae), Sida rhombifolia L. (arrow leaf sida, Family- Malvaceae), Amaranthus spinosus L. (spiny amaranth, spiny pigweed or thorny amaranth, Family-Amaranthaceae) and Centrosema pubescence Benth (centro, butterfly pea, Family-Fabaceae) were collected randomly in the month of August separately from each individual plant using well-cleaned secateurs at the various distances at the sawdust dumpsite (20, 40, 60 and 80 m) and control site (a 5 year upland bush fallow that is 500 m from the dump site where there was no visible source of contamination). Three replicates of each plant species were collected and mixed separately to obtain composite samples. These samples were well labelled and transferred to the laboratory for pretreatment and analysis. The plant samples were cleaned sequentially with deionized water to remove dust, pollens and debris and oven dried at 60 °C for 72 hrs. Thereafter, the leaf samples from each separate plant species were milled with Thomas Wiley milling machine (Model ED-5 USA) to fine powder. The procedure described by Kakulu and Jacob (2006) but slightly modified was used for digestion of plant samples. A 5 ml of 4:1 mixture of concentration of HN0₃:HCl₄ was added to 2 g of plant sample and the mixture was heated at 105 °C for an hour to dryness on a hot plate, allowed to cool and made up to the mark of 50 ml volumetric flask with 1M HNO₃. The solution was centrifuge for 30 minutes and transferred to sampling bottle for analysis. Triplicate digestion of each sample was carried out and blanks were prepared from only reagents without sample to check for background contamination by the reagents. Appropriate quality assurance procedures and precautions were taken to ensure the reliability of the results. Samples were carefully handled to avoid cross-contamination. Glassware was properly cleaned, and reagents used were of analytical grades. Deionized water was used throughout the study. Working standard solutions of chromium (Cr), zinc (Zn), cadmium (Cd), and copper (Cu) were prepared from the stock standard solutions containing 1000 ppm of element in 2N nitric acid. Calibration and measurement of elements were done on flame Atomic Absorption

Spectrophotometer, AAS (PG Instrument model: Pg-500, UK). A blank reading was also taken and necessary correction was made during the calculation of concentration of various elements.

2.5. Experimental design and data analysis

A 4 x 3 factorial experiment in Randomized Complete Block Design (RCBD) in three replicates in soil depth was used. Data collected from this study was subjected to 2-way Analysis of Variance (ANOVA) using Statistical Analysis System (SAS) version 9 to test the significance of difference in total mean concentration in sawdust, soil and plant samples and means separated using Duncan Multiple Range Test (DNMRT) at 0.05 probability level test. The correlation of heavy metals was analysed using Pearson correlation analysis.

3.0. Results and Discussion

3.1. Metal concentration (mg/kg) in sawdust

The values of the concentration of metals in samples of sawdust collected from the three (3) sawdust dumps is presented in Table 1. Sawdust concentrations of all metals were raised to different levels and the significant differences was evidenced amongst the three sawdust dumps at Ahiaeke. Wood processing at the timber market resulted to generation of metal contaminated sawdust that are dumped within the vicinity. The value for the highest concentration of Zn ($51.00 \pm 1.84 \text{ mg/kg}$) was recorded at sawdust dump 2 and the value is significantly (P < 0.05) higher than values recorded for Zn at sawdust dump 3 ($44.83 \pm 0.3535 \text{ mg/kg}$) and sawdust dump 1 ($41.06 \pm 0.226 \text{ mg/kg}$). The metal analyses of sawdust particles revealed the following properties presented in Table 1. The high value of Zn at sawdust dump 2 suggest that the sawdust were generated from trees that grew on soil rich in Zn. Plants growing on metal contaminated soil may take up metals from soils and translocate it to the stem.

Table 1: Metal concentration (mg/kg) in sawdust

Sawdust dumpsite	Zn	Cu	Cd	Cr
1	41.06 ± 0.226^{b}	8.24 ± 0.6^{a}	3.715 <u>±</u> 0.219 ^b	0.084 ± 0.0085^{b}
2	51.00 ± 1.84^{a}	6.84 ± 0.37^{a}	3.895±0.4313 ^b	0.17 ± 0.014^{a}
3	44.83±0.3535 ^b	7.82 ± 0.4^{a}	4.72 ± 0.071^{a}	0.125 ± 0.0071^{ba}

Mean in the same column followed by the same letter are not significantly different (p<0.05) according to DMRT Values are mean ± standard deviation of 3 replications

It also suggests that the sawdust at the three dumps (i.e. 1, 2 and 3) were generated from trees that grew on different sites in the wild forest or exotic plantations thus, the differences in the values of Zn at the three sawdust dumps. The values of Zn in sawdust dumps at Ahiaeke timber market range from 41.06 ± 0.226 to 51.00 ± 1.84 mg/kg which is higher than 3.54 ± 0.28 mg/kg in pine wood briquette made from planer shavings and sawdust from high quality pure pine wood (Swietlik *et al.*, 2014).

The value for the highest concentration of Cu ($8.24 \pm 0.60 \text{ mg/kg}$) was recorded at dump 1 but the value is statistically equal (P > 0.05) to its corresponding values at sawdust dump 2 ($6.84 \pm 0.37 \text{ mg/kg}$) and sawdust dump 3 ($7.82 \pm 0.40 \text{ mg/kg}$). The values of Cu at the three dumps suggest that the sawdust were likely generated from trees harvested from the same sites (i.e. location) or sites with similar edaphic nature. The values of Cu in sawdust dumps range from 6.84 ± 0.37 to $8.24 \pm 0.60 \text{ mg/kg}$ which is higher than $0.65 \pm 0.08 \text{ mg/kg}$ in pine wood briquette made from planer shavings and sawdust from high quality pure pine wood (Swietlik *et al.*, 2014).

The value for the highest concentration of Cd ($4.72 \pm 0.071 \text{ mg/kg}$) was recorded at sawdust dump 3 and the value is significantly (P < 0.05) higher than values of Cd at sawdust dump 1 ($3.715 \pm 0.219 \text{ mg/kg}$) and sawdust dump 2 ($3.895 \pm 0.4313 \text{ mg/kg}$). The high Cd at sawdust dump 3 is attributed to Cd assimilated by the trees (via the roots) while taken up macronutrients from soil solution. The Cd assimilated in such trees were released in form of sawdust particles while been processed at the Ahiaeke timber market and possibly disposed at sawdust dump 3. The values of Cd in sawdust dumps range from 3.715 ± 0.219 to $4.720 \pm 0.071 \text{ mg/kg}$ which is higher than 0.50 mg/kg reported in sawdust particles in the vicinity of sawmill in Sapele, Nigeria (Nwajei and Iwegbue, 2007).

The value for the highest concentration of Cr $(0.170 \pm 0.014 \text{ mg/kg})$ was obtained at sawdust dump 2 and the value is significantly (P < 0.05) higher than value observed at sawdust dump 1 (0.084 ± 0.0085 mg/kg) but statistically equal (P > 0.05) to the value of Cr at sawdust dump 3 (0.125 ± 0.0071 mg/kg).

The main source of Zn, Cu and Cr in sawdust particles of Ahiaeke timber market are the chemicals used in pest and disease control in various man-made forest plantations. Pesticides such as copper sulphate, Boliden salt (BIS-salt) mixed with zinc sulphate and chromate copper arsenate (CCA) have been used for over five decades (Bahattacharya et al. 2002). The values of Cr in sawdust dumps range from 0.084 \pm 0.0085 to 0.170 \pm 0.014 mg/kg which is well below 1.46 to 160.50 mg/kg in sawdust particles in the vicinity of sawmill in Sapele, Nigeria (Nwajei and Iwegbue, 2007). The values of Cr $(0.084 \pm 0.0085 \text{ to } 0.170 \pm 0.014 \text{ mg/kg})$, Cd $(3.715 \pm 0.219 \text{ to } 4.720 \pm 0.071 \text{ mg/kg})$ and Cu $(6.84 \pm 0.0085 \text{ to } 0.170 \pm 0.014 \text{ mg/kg})$ 0.37 to 8.24 ± 0.60 mg/kg) in the three sawdust dumps at Ahiaeke timber market are well below the maximum permitted levels of 25 mg/kg (Cr), 50 mg/kg (Cd) and 40 mg/kg (Cu) established by the Waste and Regeneration Action Program and the British Standard Institution (BSI, 2012). Thus, the sawdust is safe for panel board manufacturing. Similarly, the values of the metals are well below the maximum permitted levels of 100 mg/kg (Cr), 200 mg/kg (Cu) and 400 mg/kg (Zn) except for Cd that is higher than 1.5 mg/kg (Cd) for porous surface application (BSI, 2012) of sawdust in soil. Notwithstanding this, persistent application of the sawdust for composting and mulching over time (i.e. years) can trigger the concentrations of the metals (Cr, Cd, Zn and Cu) to and above the maximum permitted levels in agricultural lands. Generally, the concentration of the metals in sawdust particles followed a decreasing order: Zn > Cu > Cd > Cr.

3.2. Metals concentration (mg/kg) in soil

The values of the concentration of metals in different soil depths at the various distances at timber market sawdust dumpsite are presented in Table 2. The results show that the highest and lowest metal concentrations in soil were observed at the dumpsite and control site, respectively. Investigations on some pollution surveys showed that air, soil or plants adjoined to source of pollutants had elevated metal concentrations than the control area (Imperatoa et al., 2003; Moreno et al., 2003; Birch and Snowdon, 2004; Davila et al., 2006). Since there were no other sources of contamination in the area, the high concentrations of metals in soils of the sawdust dumpsite (unlike the control site) may be attributed to leaching of these metals (Cd, Zn, Cu and Cr) from the mountainous sawdust waste. Ncube and Phiri (2015) reported presence of metals in Eucalyptus and Pinus wood sawdust and smoke in Copperbelt province, Zambia. Nwajei and Iwegbue (2007) also reported some heavy metals in sawdust particles in the vicinity of sawmill in Sapele, Nigeria. Consequently, sawdust can influence the natural concentrations of heavy metals in soil. Copper fungicides and other forms of pesticides used to control disease infection and pest infestation in exotic plantations (e.g. Gmelina arborea. Pinus caribea, Eucalyptus camadulensis, Tectona grandis among others) may have contributed to metal load in soil and subsequent accumulation in the trees. Mala et al. (2007) in their study of heavy metal uptake in plants reported heavy metals in the anatomical features of stem. From the study, it was observed that the values of metals decreased with soil depth at the timber market sawdust dumpsite.

The magnitude of decline in metals concentration with depth in this study varied amongst sampling distance (20, 40, 60 and 80 m) and control area but the rate of decline were highest at the control area, followed by 80 m, 60 m, 40 m, and lastly 20 m. The high concentration of Zn, Cu, Cd and Cr in 0-10 cm depth at various distances is attributed to organic materials on the surface soil. Metals are bound to topsoil by organic matter (Sukkariyah *et al.*, 2005) because they (metals) are complexed, hence reducing the leaching of metals into the lower depths (i.e. 11 - 20 and 21 - 30 cm). It was also observed that the values of metals at the timber market sawdust dumpsite area decreased exponentially with distance. Such non-linear decreasing metal concentrations in soils with increasing distance to the emission source have been reported in a similar study (Escarré *et al.*, 2010). This suggests that sawdust is the source of metals leached across the various distances where soil samples were tested in this study. Liang *et al.* (2003) opined that transfer through water runoff is the main vehicle of heavy metals transportation in soil.

Distance	Depth (cm)	Zn	Cu	Cd	Cr
(m)					
20	0-10	119.7 ± 7.02 ^a	75.85 ± 4.8^{a}	22.39 ± 3.3^{a}	0.8 ± 0.07^{a}
	11-20	89.4 ± 9.01^{b}	53.63 ± 2.3^{b}	13.72 ± 1.52^{c}	0.55 ± 0.47^{abc}
	21-30	67.36±4.06 ^c	36.67 ± 2.96^{d}	7.93±1.66 ^e	0.27 ± 0.05^{bcd}
40	0-10	82.01 ± 7.97^{b}	48.36±3.34 ^c	16.90 ± 1.94^{b}	0.641 ± 0.03^{ab}
	11-20	70.42 ± 6.24^{c}	31.27 ± 1.15^{e}	10.62 ± 1.14^{d}	0.35 ± 0.03^{bcd}
	21-30	56.99 ± 9.00^{d}	21.92 ± 1.95^{f}	4.95±4.0.71 ^g	0.19 ± 0.03^{bcd}
60	0-10	63.42. ±7.82 ^{cd}	31.18 ± 1.19 ^e	11.55 ± 1.59^d	0.39 ± 0.03^{abc}
	11-20	56.16±8.61 ^{cd}	23.74 ± 4.39^{f}	6.27 ± 1.17^{f}	0.22 ± 0.05^{bcd}
	21-30	39.1±9.42 ^e	18.36±2.99 ^g	3.15 ± 1.35^{h}	0.12 ± 0.04^{cd}
80	0-10	49.56 ± 5.14^{d}	22.96 ± 1.64^{f}	4.76 ± 0.36^{g}	0.15 ± 0.03^{cd}
	11-20	35.48±11.78 ^e	17.37 ± 1.09 ^g	1.35 ± 0.47^{i}	0.09 ± 0.03^{d}
	21-30	25.49 ± 7.35^{fe}	11.86 ± 0.81^{h}	0.48 ± 0.16^{i}	0.05 ± 0.03^{d}
Control	0-10	31.26 ± 3.23 ^e	18.18 ± 2.27 ^g	0.29 ± 0.11^{ij}	0.01 ± 0.01^{d}
	11-20	19.08 ± 2.94^{f}	11.06 ± 1.40^{h}	0.11 ± 0.05^{ij}	0.00 ± 0.00^{d}
	21-30	10.11±0.97 ^{gf}	6.80±1.59 ⁱ	0.02 ± 0.02^{j}	0.00 ± 0.00^d

Table 2: Metals concentration (mg/kg) in soil samples

Mean in the same column followed by the same letter are not significantly different (p<0.05) according to DMRT Values are mean ± standard deviation of 3 replications

The concentration of Zn (119.7 \pm 7.02 mg/kg), Cu (75.85 \pm 4.80 mg/kg) and Cd (22.39 \pm 3.30 mg/kg) in 0 - 10 cm at a distance of 20 m to the timber market sawdust dumpsite is significantly (P < 0.05) higher than their corresponding values at 40 m (82.01 ± 7.97 , 48.36 ± 3.34 and 16.90 ± 1.94 mg/kg), $60 \text{ m} (63.42 \pm 7.82, 31.18 \pm 1.19 \text{ and } 11.55 \pm 1.59 \text{ mg/kg})$, $80 \text{ m} (49.56 \pm 5.14, 22.96 \pm 1.64 \text{ and } 4.76 \text{ mg/kg})$ \pm 0.36 mg/kg) and control (31.26 \pm 3.23, 18.18 \pm 2.27 and 0.29 \pm 0.11 mg/kg). The metals present in the timber market sawdust dumpsite may have provided a source for continued dispersion down the distance, and have resulted to various degree of contamination in soils. The concentrations of Zn, Cu and Cd in 0 - 10 cm depth at a distance of 20 m were found to be 1.46, 1.57 and 1.32 times higher than their values in 0 - 10 cm at 40 m; 1.89, 2.43 and 1.94 times higher than their values at 60 m; 2.42, 3.30 and 4.70 times higher than their values at 80 m; and 3.83, 4.17 and 77.21 times higher than their values at the control area, respectively for Zn, Cu and Cd. The concentration of these metals at the study area is well above their concentrations at the control area. Logan and Miller (1983) suggested that soil is contaminated when concentrations of metals in soils were two-to-three times higher than the control. In this study, the concentrations of Zn, Cu and Cd were more than three times higher than their concentrations at the control area. Therefore, the soil at the timber market sawdust dumpsite area can be said to be contaminated based on the findings that Zn, Cu and Cd concentrations in the control soil samples were well below their corresponding values at the study area.

The values of the concentration of Zn, Cu and Cd in timber market soils of Ahiaeke, Abia State, Nigeria were 25.49 ± 7.35 to 119.7 ± 7.02 , 11.86 ± 0.81 to 75.85 ± 4.80 and 0.48 ± 0.16 to 22.39 ± 3.30 mg/kg, respectively for Zn, Cu and Cd, which are above the maximum permitted levels of 60 mg/kg (Zn) and 0.1 mg/kg (Cd) established by the Codex Alimentarius Commission (FAO/WHO, 2001) (Table 3). Similarly, the concentrations of Cu (11.86 ± 0.81 to 75.85 ± 4.80 mg/kg) and Cd (0.48 ± 0.16 to 22.39 ± 3.30 mg/kg) in soils at the timber market sawdust dumpsite area is above the accepted limits (i.e. target value) of 36 mg/kg (Cu) and 0.8 mg/kg (Cd) as described by Dutch criteria for soil (Wikipedia, 2013).

Table 3: Comparison of results with International Standard (Dutch Criteria and FAO/WHO Codex

 Alimentarius Commission

	Dutch criteria (target value) mg/kg	FAO/WHO 2001 Codex Alimentarius Commission (mg/kg)	NESREA 2011 Standard (mg/kg)
Zn	140	60	421
Cu	36	100	100
Cd	0.8	0.1	3
Cr	100	100	100

The highest concentration of Cr $(0.80 \pm 0.07 \text{ mg/kg})$ in 0 - 10 cm depth at 20 m is statistically equal (P > 0.05) with the values recorded in 0 - 10 cm depth at 40 m (0.641 ± 0.03 mg/kg) and 60 m (0.39 ± 0.03 mg/kg) but significantly (P < 0.05) higher than 0.15 ± 0.03 mg/kg at 80 m and 0.01 ± 0.01 mg/kg

at control area. The values of Cr (0.05 ± 0.03 to 0.80 ± 0.07 mg/kg) is well below the permitted limit of 100 mg/kg (Cr) established by the Codex Alimentarius Commission (FAO/WHO, 2001) (Table 3) and Dutch criteria for soil (Wikipedia, 2013). The values of Zn is 25.49 ± 7.35 to 119.7 ± 7.02 mg/kg at the timber market sawdust dumpsite area, which is well above 3.58 to 9.19 mg/kg for Zn in soils at sawmills in Ekiti State, Nigeria (Ezekiel *et al.*, 2013). The values of Cu (11.86 ± 0.81 to 75.85 ± 4.80 mg/kg) in this study are higher than 0.76 to 3.54 mg/kg (Ezekiel *et al.*, 2013) in a similar study. Similarly, the value of Cd (0.48 ± 0.16 to 22.39 ± 3.30 mg/kg) is higher than 0.07 to 0.47 mg/kg reported by Ezekiel *et al.* (2013) but the values of Cr (0.05 ± 0.03 to 0.80 ± 0.07 mg/kg) in this study is well below 0.68 to 3.34 mg/kg for Cr in soils at sawmills in Ekiti State (Ezekiel *et al.*, 2013). Generally, the values of the concentrations of metals in soil followed an increasing order: Cr < Cd < Cu < Zn.

3.3. Metals concentration (mg/kg) in plants

The values of the concentration of metals tested in plant samples in this study are summarized in Table 4. The result indicates that the highest and lowest values of the concentration of metals were observed at the sawdust dumpsite and control site, respectively. The table shows that the plant species assimilated different levels of concentration of metals at various distances from the emission source (i.e. sawdust dumps). The result clearly indicate that *Centrosema pubescence* assimilated the highest values of Zn (34.70 \pm 7.05 mg/kg), Cu (5.34 \pm 0.11 mg/kg) and Cd (2.94 \pm 0.515 mg/kg) but the values are statistically equal (P > 0.05) to the values of Zn, Cu and Cd in *Eleusine indica* (30.90 \pm 7.70, 4.87 \pm 1.20 and 2.92 \pm 0.60 mg/kg) and 28.50 \pm 6.74 mg/kg Zn in Amaranthus spinosus but significantly (P < 0.05) higher than values of Zn, Cu and Cd, respectively for *Eleusine indica*, Sida rhombifolia, Amaranthus spinosus and Centrosema pubescence at 40 m (22.07 \pm 5.93, 3.106 \pm 0.23 and 1.80 ± 0.28 mg/kg; 15.51 ± 7.30 , 2.16 ± 0.73 and 1.04 ± 0.575 mg/kg; 16.25 ± 5.46 , 1.90 ± 0.20 and 1.06 ± 0.46 mg/kg; and 23.79 ± 4.01 , 3.70 ± 0.337 and 1.78 ± 0.44 mg/kg), 60 m (10.11 ± 3.14 , 2.183 ± 0.30 and 1.05 ± 0.11 mg/kg; 7.75 ± 6.58 , 1.14 ± 0.30 and 0.51 ± 0.11 mg/kg; 7.05 ± 8.032 , 1.47 ± 0.13 and 0.82 ± 0.09 mg/kg; and 10.89 ± 2.73 , 2.39 ± 0.45 and 1.13 ± 0.072 mg/kg), 80 m $(3.49 \pm 1.70, 1.10 \pm 0.98 \text{ and } 0.577 \pm 0.04 \text{ mg/kg}; 2.30 \pm 1.10, 0.903 \pm 0.12 \text{ and } 0.45 \pm 0.19 \text{ mg/kg};$ 2.63 ± 0.16 , 0.95 ± 0.63 and 0.413 ± 0.071 ; and 3.67 ± 2.00 , 1.13 ± 0.14 and 0.52 ± 0.01 mg/kg) and the control $(1.17 \pm 0.54, 0.23 \pm 0.095 \text{ and } 0.010 \pm 0.11; 0.61 \pm 0.95, 0.096 \pm 0.08 \text{ and } 0.021 \pm 0.003$ mg/kg; 0.49 ± 0.06 , 0.22 ± 0.078 and 0.013 ± 0.0013 mg/kg; and 1.540 ± 0.71 , 0.38 ± 0.10 and 0.020 ± 0.005 mg/kg). The high values of Zn, Cu and Cd in C. pubescence may be attributed to the inherent ability of the plant (C. pubescence) to absorb and translocate more Zn, Cu and Cd to the aerial plant parts (leaves) than other plant species. Its deep root system (Wikipedia, 2018) might have facilitated the absorption of the metals in soil solution from a significant depths and translocation to the aerial part of the plant. Metal accumulation in plants is dependent on type of metal and plant species involved (Juste and Mench, 1992; Ogbonna and Okezie, 2011).

The value of the concentration of Zn increased from $2.30\pm1.10 \text{ mg/kg}$ (S. rhombifolia) at 80 m to $34.70 \pm 7.05 \text{ mg/kg}$ (C. pubescence) at 20 m. The level of Zn in this study is below the permissible limit (PL) of 50 mg/kg set by Codex Alimentarius Commission, FAO/WHO (2006) for vegetables and herbs. The value of Zn in C. pubescence at 20 m is 22.53 times higher than the highest value of Zn in plant at the control site. The value of the concentration of Cu increased from 0.903 ± 0.12 mg/kg (S. *rhombifolia*) at 80 m to 5.345 ± 0.11 mg/kg (*C. pubescence*) at 20 m. The level of Cu is lower than the permissible limit (PL) of 40 mg/kg set by FAO/WHO (2006) for vegetables and herbs. The value of Cu in C. pubescence at 20 m is 14.07 times higher than the highest value of Cu in plant at the control site. The value of the concentration of Cr increased from 0.0037 ± 0.0055 mg/kg (C. pubescence) at 80 m to 0.132 ± 0.01 mg/kg (*C. pubescence*) at 40 m. The level of Cr is lower than the permissible limit (PL) of 2.3 mg/kg set by FAO/WHO (2006) for vegetable and herbs. The value of Cr in C. pubescence at 40 m is 0.132 times higher than the highest value of Cr in plant at the control site. The value of the concentration of Cd increased from 0.413 \pm 0.071 (S. rhombifolia) at 80 m to 2.94 \pm 0.515 mg/kg (C. pubescence) at 20 m. The level of Cd in this study is well above the permissible limit (PL) of 0.3 mg/kg set by FAO/WHO (2006) for vegetables and herbs. Consequently, the use of C. pubescence at the timber market for forage and source of protein for grazing animals can be a route of entry of metal (Cd) in herbivores and subsequent bio-magnification of Cd in people that consume such metal contaminated animals. In furtherance to this, collection of planting material for growing as cover crops from such Cd contaminated C. pubescence will hamper soil fertility and health of soil organism such as earthworm. The value of Cd in *C. pubescence* at 20 m is 140 times higher than the highest value of Cd in plant at the control site. According to FAO (1991), sawmill wastes contain significant spectrum of organic substances capable of affecting the physical, chemical and biotic environment. Consequently, consumption of plants, animals or water contaminated with such substances can be deleterious to human health. Generally, the values of the concentration of metals followed an increasing order: Cr < Cd < Cu < Zn.

Distance (m)	Plant species	Zinc	Cu	Cd	Cr
20	E. indica	30.9 ± 7.70^{a}	4.87 ± 1.20^{a}	2.92 ± 0.60^{a}	0.05 ± 0.009^{b}
	S. rhombifolla	23.9 ± 6.35^{b}	3.173 ± 0.68^{bc}	$1.89 \pm 0.42^{\circ}$	0.04 ± 0.007^{b}
	A. Spinosus	28.5 ± 6.74^{ab}	3.57 ± 1.35^{b}	2.3 ± 0.41^{bc}	0.039 ± 0.021^{b}
	C.pubescen	34.7 ± 7.05^{a}	5.345 ± 0.11^{a}	2.94 ± 0.515^{a}	0.037 ± 0.18^{b}
40	E. indica	22.07 ± 5.93^{bc}	3.016 ± 0.23^{bc}	$1.8 \pm 0.28^{\circ}$	0.0243 ± 0.005^{b}
	S. rhombifolla	15.51 ± 7.3^{cd}	2.16 ± 073^{d}	1.04 ± 0.575^{d}	0.0273 ± 0.01^{b}
	A. Spinosus	16.25 ± 5.46^{cd}	1.9 ± 0.20^{d}	1.06 ± 0.46^{d}	0.05 ± 0.04^{b}
	C.pubescen	23.79 ± 4.01^{b}	3.7 ± 0.337^{b}	$1.78 \pm 0.44^{\circ}$	0.132 ± 0.013^{a}
60	E. indica	10.11 ± 3.14^{de}	2.183 ± 0.3^{d}	1.05 ± 0.11^{d}	0.044 ± 0.048^{b}
	S. rhombifolla	$7.75 \pm 6.58^{\text{ef}}$	1.14 ± 0.3^{e}	0.51 ± 0.11^{def}	0.054 ± 0.059^{b}
	A. Spinosus	$7.05 \pm 8.032^{\text{ef}}$	1.47 ± 0.13^{de}	0.82 ± 0.09^{de}	0.037 ± 0.037^{b}
	C.pubescen	10.89 ± 2.73^{de}	$2.39 \pm 0.45^{\circ}$	1.13 ± 0.072^{d}	0.043 ± 0.04^{b}
80	E. indica	$3.49 \pm 1.70^{\text{fg}}$	1.10 ± 0.98^{ef}	$0.577 \pm 0.04^{\text{def}}$	0.007 ± 0.05^{b}
	S. rhombifolla	$2.3 \pm 1.10^{\text{fg}}$	$0.903 \pm 0.12^{\text{ef}}$	$0.45 \pm 0.19^{\text{ef}}$	0.004 ± 0.06^{b}
	A. Spinosus	$2.63 \pm 0.16^{\text{fg}}$	$0.95 \pm 0.63^{\text{ef}}$	$0.413 \pm 0.071^{\text{ef}}$	0.0071 ± 0.0051^{b}
	C.pubescen	$3.67 \pm 2.00^{\text{fg}}$	1.13 ± 0.14^{e}	$0.52 \pm 0.01^{\text{def}}$	0.0037 ± 0.0055^{b}
Control	E. indica	$1.17 \pm 0.54^{\text{fg}}$	$0.23 \pm 0.095^{\text{fg}}$	$0.010 \pm 0.11^{\text{f}}$	ND
	S. rhombifolla	0.61 ± 0.95^{g}	0.096 ± 0.085^{g}	$0.021 \pm 0.003^{\text{f}}$	ND
	A. Spinosus	0.49 ± 0.06^{g}	$0.22 \pm 0.078^{\text{fg}}$	0.013 ± 0.0013^{f}	ND
	C.pubescen	1.540 ± 0.71^{g}	$0.38 \pm 0.10^{\text{fg}}$	$0.020 \pm 0.005^{\text{f}}$	ND

Table 4: Metals concentration (mg/kg) in plant samples

Mean in the same column followed by the same letter are not significantly different (p<0.05) according to DMRT Values are mean \pm standard deviation of 3 replications

4.0 Conclusion

The results of this work showed that sawdust particles at Umuahia timber market contain Zn, Cr, Cu and Cd and their concentration are within the safe limit. It was discovered that the sawdust is safe for mulching and production of wood panels. The highest concentration of metals occurred at the surface soil and the levels of Zn and Cd exceeded the permissible limit set by Codex Alimentarius Commission and Dutch criteria for soil. Similarly, the value of the concentration of Cd in *Centrosema pubescence* exceeded the permissible limit established by the Codex Alimentarius Commission. Thus, the *C. pubescence* can be used for phytoremediation of the metal contaminated site only on the condition that it will not be fed to animals or used for medicinal purposes by man.

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