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Impact of Saw Dust Application on the Distribution of Potentially Toxic Metals in Contaminated Soil

Emmmanuel E. Awokunmi[1]

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Abstract The need to develop an approach for the reclamation of contaminated site using locally available agricultural waste has been considered. The present study investigated the application of sawdust as an effective amendment in the immobilization of potentially toxic metals (PTMs) by conducting a greenhouse experiment on soil collected from an automobile dumpsite. The amended and non-amended soil samples were analyzed for their physicochemical parameters and sequential extraction of PTMs. The results revealed that application of amendment had positive impact on the physicochemical parameters as organic matter content and cation exchange capacity increased from 12.1% to 12.8% and 16.4 to 16.8 meq/100 g respectively. However, the mobility and bioavalability of these metals was reduced as they were found to be distributed mostly in the non-exchangeable phase of soil. Therefore, application of sawdust successfully immobilized PTMs and could be applied for future studies in agricultural soil reclamation.

Keywords Reclamation · Agricultural soil · Field application · Saw dust

Potentially toxic metals (PTMs) pollution of soil due to intense industrialization and urbanization has become a serious concern in many developing countries (Mireles et al. 2012; Yaklali-Abamuz 2011). Contamination of soil by PTMs can limit the usability of land for agricultural production by adversely affecting crop growth and food quantity. PTMs are known to be phytotoxic and ecotoxic as they enter into the food chain through absorption by plant's root (McLaughlin et al. 2000; Ling et al. 2007).

The need for good agricultural soils for improved agricultural practices has necessitated research into the immobilization of PTMs. Over the last few decades, a great deal of researches have been carried out in order to develop strategies for the management of agricultural ecosystems (Chukwuka and Omotayo 2008), as well as remediation of former industrial sites, which have been exposed to intense pollution by PTMs (Belviso et al. 2010). Among the remediation technologies available, immobilization of heavy metals is more advantageous since they are generally less expensive and disruptive to material landscape, hydrology and ecosystem, compared to conventional methods such as excavation, soil washing, desorption and air stripping (Lombi et al. 2004; Bolan et al. 2005).

Recently, the application of biochar as soil amendment gained attention because of its potential soil conditioning properties brought about by beneficial physico-chemical characteristics (Luke et al. 2014). One of these important physicochemical characteristics is high organic matter (Yin-Chan and Xu 2009), which encourages its ability to sequester heavy metals (Lehmann 2007a, b). As a result of these, it is important to identify other organic materials that could be applied as amendment in the immobilization of PTMs on historically contaminated sites.

This present study was focused on the application of sawdust as an effective amendment in the immobilization of PTMs and its possible future field application.

✉ Emmmanuel E. Awokunmi
emmanuel.awokunmi@eksu.edu.ng

[1] Department of Chemistry, Faculty of Science, Ekiti State University, PMB 5363, Ado Ekiti, Nigeria

Materials and Methods

Soil samples were collected randomly (0–30 cm depth) from ten locations each on the south and north of automobile dumpsite located in Akure South local government, Ondo State, Nigeria. Control samples were collected in the same manner at 500 m away from the last collection point on the south and north coordinates of the dumpsite. The dumpsite which has existed for over 20 years is located on Latitude 7.26°N and 5.21°E. 4 kg of the samples were sieved using 0.2 mm mesh and thoroughly mixed with 1 kg of sawdust obtained from *Gmenlina arborea* in plastic pots and in another pot 5 kg of soil without amendment as control, according to the method prescribed by Luke et al. (2014). The sawdust was analyzed with the following concentrations of PTMs; Co(0.16 ± 0.03), Zn(0.87 ± 0.02), Cu(1.25 ± 0.22), Fe(2.80 ± 0.38) all in mg/kg; Cr, Pb, and Zn were not detected. After addition of the amendment, the potted soil was watered with distilled/deionized water to approximate field capacity and was allowed to incubate for 4 months in a greenhouse. The pots were placed in individual trays to prevent loss of amendment and other components by leaching.

The soil pH and organic matter content (loss on ignition) were determined according to the methods of Hong and Teresa (2001). Cation exchange capacity was determined by a method described by Jackson (1962). The digestion method prescribed by Ncube and Phiri (2015) was used for the saw dust and soil samples before analysis of PTMs with atomic absorption spectrophotometer (AAS, Perkin Elmer Model 306).

The sequential extraction techniques adopted for this study (Table 1) was a 5-step approach employed by Tessier et al. (1979).

Results and Discussion

The results of physicochemical parameters of non-amended and amended contaminated soil are depicted in Table 2. There was observable increase in pH values from 6.85 to 7.20 resulting from application of amendment. The soil pH is one of the important factors affecting the mobility and bioavailability of PTMs; as most of the PTMs are rendered less mobile and less available for plants' uptake if the soil pH is kept near neutral or above (Ismail et al. 2005).

Table 2 Results of physicochemical parameters of contaminated soil with and without amendment

	pH	OMC (%)	CEC (meq/100 g)
Non amended 1 (n = 10)	6.8 ± 0.02	12.1 ± 0.01	16.5 ± 0.03
Non amended 2 (n = 10)	6.9 ± 0.01	12.8 ± 0.02	16.8 ± 0.01
Mean	6.85	12.45	16.65
Amended (n = 10)	7.2 ± 0.03	18.2 ± 0.01	21.8 ± 0.02

OMC organic matter content, *CEC* cation exchange capacity

The organic matter content of locations on the automobile dumpsites ranged from 12.1% to 12.8% before application of amendment, with an average of 12.45%. Application of amendment also increased the percentage organic matter to 18.2. Organic matter makes strong complexes with PTMs. Solid organic matter is for example able to hold metals in the solid phase of the soil. As organic materials influence the binding of PTMs in soil, it may also affect plant uptake (Baker et al. 2013).

The cation exchange capacity of locations on the dumpsite ranges from 16.5 to 16.8 meq/100 g, with an average value of 16.5 meq/100 g. The cation exchange capacity increased after the application of amendment from an average value of 16.65 meq/100 g to 21.80 meq/100 g. This considerable increase in the cation exchange capacity of the soil samples is due to the presence of more negatively charged species in the amendment which increases the density of the negative charges on the soil surface so as to balance the cations in the soil to maintain electro-neutrality (Fabio and Reinaldo 2012).

Table 3 shows the concentrations of PTMs in the soil samples from locations on the automobile dumpsite before and after the application of amendment. The results revealed that concentration of Co ranged from 180.0 to 190.0 mg/kg, with an average value of 185.0 mg/kg. Many studies have shown that urban soils receives loads of contaminants that are usually greater than the surrounding sub-urban or rural areas due to the concentration of anthropogenic activities

Table 1 Sequential extraction procedure

Fraction	Solution	Equilibrium conditions
Exchangeable	8 mL 1 M $MgCl_2$ (pH 7)	1 h, room temperature
Carbonates	8 mL 1 M NaOAc (pH 5)	5 h, room temperature
Fe and Mn oxides	20 mL 0.04 M NH_2OH/HCl in 25% (v/v) HOAc	6 h, 96 °C
Organic matter	3 mL 0.02 M HNO_3 + 5 mL 30% H_2O_2 (pH 2)	3 h, 85 °C
	5 mL 3.2M NH_4OAC in 20% (v/v HNO_3 + 7 mL water)	20 min, room temperature
Residual	HNO_3-HCl digestion	

Table 3 Concentration of potentially toxic metals in non amended and amended soil

	Co	Cr	Pb	Zn	Cu	Ni	Fe
Non amended 1 (n = 10)	190.0 ± 0.02	200.0 ± 0.08	11.0 ± 0.01	136.0 ± 0.01	166.0 ± 0.02	60.0 ± 0.01	1380.0 ± 0.1
Non amended 2 (n = 10)	180.0 ± 0.01	140.0 ± 0.03	6.0 ± 0.01	119.0 ± 0.06	103.0 ± 0.01	90.0 ± 0.01	1970.0 ± 0.2
Mean	185.0	170.0	8.5	127.5	134.5	75.0	1675.0
Amended 1 (n = 10)	230.0 ± 0.1	310.0 ± 0.02	13.0 ± 0.02	168.0 ± 0.02	201.0 ± 0.02	90.0 ± 0.03	1900.0 ± 0.1
Amended 2 (n = 10)	240.0 ± 0.01	260.0 ± 0.04	9.0 ± 0.03	125.0 ± 0.04	131.0 ± 0.03	130.0 ± 0.04	2310.0 ± 0.2
Mean	235.0	285.0	11.0	146.5	166.0	110.0	2105.0

of urban settlements (Charlesworth et al. 2003). The values of Co obtained in this study were lower than ones reported by Awokunmi et al. (2010) in soil from selected dumpsites located within Ikere and Ado-Ekiti, South West Nigeria. The higher levels found could be attributed to indiscriminate disposal of Co containing wastes on the dumpsite. The concentration of Co increased after the application of amendment to the top location and bottom location soil samples having a range of 230.0–240.0 mg/kg with an average value of 235.0 mg/kg; thus indicating that the application of amendment increased the concentration of Co.

The concentration of Cr in the soil ranged from 140.0 to 200.0 mg/kg with an average value of 170.0 mg/kg. The concentrations of Cr obtained were lower than that reported by Adefemi and Awokunmi (2009) in dumpsites within Ado-Ekiti town in South West Nigeria. The elevated concentrations were ascribed to deposited wastes which contained high concentration of Cr. In the amended top and bottom location soil samples, the concentration of Cr ranged from 260.0 to 310.0 mg/kg with an average value of 285.0 mg/kg.

The concentration of Pb in the top and bottom locations ranged from 6.0 to 11.0 mg/kg with an average value of 8.5 mg/kg. The result showed a significant variation in the concentration of Pb in the two locations with a difference of 5.0 mg/kg. The results obtained in this work are lower than values reported by Adelekan and Abegunde (2011), which investigated the occurrence of heavy metals at automobile mechanic villages in Ibadan with reported Pb concentration ranging from 18.25 to 15,100 mg/kg in the soil. The concentration of Pb in the soil samples after the application of amendment ranged from 9.0 to 13.0 mg/kg with an average value of 11.0 mg/kg.

The concentration of Ni in the top and bottom locations ranged from 60.0 to 90.0 mg/kg with an average value of 75.0 mg/kg. The values reported in this work are similar to those obtained by Awokunmi et al. (2010). Ni content in soil can be as low as 0.2 mg/kg or as high as 450 mg/kg; although the average is about 20 mg/kg (Lenntech 2009). After the application of amendments to the soil samples, Ni concentration increased within the range of 90.0-130.0 mg/kg with an average value of 110.0 mg/kg.

The concentration of Zn in the soil samples before the addition of amendment ranged from 119.0 to 136.0 mg/kg with an average of 127.5 mg/kg. The application of amendment to the soil samples increased Zn concentration to range of 125.0–168.0 mg/kg with an average value of 146.5 mg/kg. The result showed considerable variation in the soil samples of the top and bottom locations, which may be due to lateral variation in the distribution of metals in the soil. However the concentrations of Zn in this study were lower compared with many other studies (Nwachukwu et al. 2010; Shinggu et al. 2007).

Cu was detected in both the top and bottom locations of the automobile dumpsite with concentration ranging from 103.0 to 166.0 mg/kg and an average value of 134.5 mg/kg. The concentration of Cu increased to a range of 131.0–201.0 mg/kg with an average value of 166.0 mg/kg after the application of amendment. These values exceeded the maximum allowable limit of 100 mg/kg (Lacatusu 2000).

The concentrations of Fe in the top and bottom locations was in the range of 1380.0–1970.0 mg/kg with an average value of 1675.0 mg/kg; thus showing significant variation in the concentration of Fe in the two sample locations with a difference of 590.0 mg/kg. The high concentration of Fe was due to leaching of scrap automobile parts in the soil since larger percentage of automobile parts were made from it. This result is higher than that reported by Fagbote and Olanipekun (2010) and Adefemi and Awokunmi (2009) on soils in Nigeria.

The water extractable concentrations of PTMs (Table 4) were determined for comparison of the reproducibility of the results of metals in the exchangeable phase of amended and non-amended soil. From the results, it was revealed the concentrations of PTMs were comparatively higher in amended soil than non-amended soil. The higher concentrations of PTMs in the amended soils are attributed to the presence of these metals in amendment. The mean concentrations of the PTMs where found in the order: Fe (59.7) > Zn (51.5) > Cu

Table 4 Concentration of water extractable PTMs in non-amended and amended soil (mg/kg)

n = 10	Co	Cr	Pb	Zn	Cu	Ni	Fe
1a	19.0 ± 0.01	26.2 ± 0.02	3.3 ± 0.01	46.2 ± 0.01	38.2 ± 0.02	10.6 ± 0.01	56.6 ± 0.07
2a	17.8 ± 0.02	15.1 ± 0.02	3.2 ± 0.01	56.8 ± 0.05	36.8 ± 0.03	13.8 ± 0.03	62.7 ± 0.01
Mean	18.4	20.7	3.3	51.5	37.5	12.2	59.7
1b	23.2 ± 0,01	38.6 ± 0.03	3.8 ± 0.01	48.2 ± 0.02	42.4 ± 0.03	12.2 ± 0.02	82.7 ± 0.03
2b	26.6 ± 0.03	27.8 ± 0.01	3.8 ± 0.01	76.2 ± 0.04	39.2 ± 0.02	14.8 ± 0.02	96.2 ± 0.02

(37.5) > Cr (20.7) > Co (18.4) > Ni (12.2) > Pb (3.3), all in mg/kg in the non-amended soil. Similar trends of results were obtained for the amended soil. The water extractable PTMs is one of the important tools to measure mobility and bio-availability, as solubility of these metals is directly related to mobility. Awokunmi et al. (2015) reported that the higher the mobility of metals the more the tendencies for availability and the resultant bio- accumulation by plant. Hence, there is need to carry out the sequential extraction of PTMs in these soil so as to provide more information on their phase distribution and mobility.

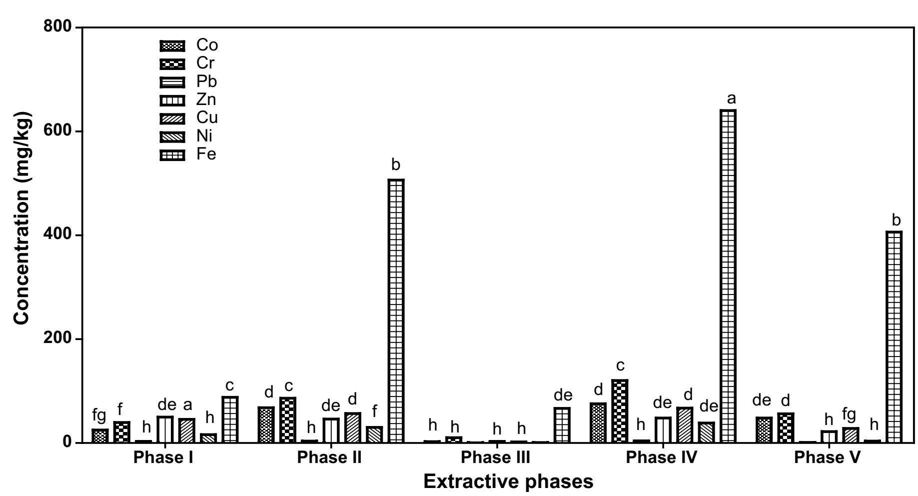
The sequential extraction procedures prescribed by Tessier et al. (1979) was employed to determine the extent of distribution of the PTMs considered in this study into different phases of soil. This technique assisted in classifying metals in soil as non-mobile and mobile phases as metals associated with exchangeable phase (phase I) of soil are considered to be the most mobile potentially toxic metal (Figs. 1, 2). The mobility of PTMs decreased from the exchangeable phase of soil to the residual phase, this resulted in the decrease in the levels of metals available for plant uptake. This was further attested to by the results presented in Table 5 as there were considerable decreases in % mobility of amended as compared to non-amended soils. Studies have revealed that bioavailability of PTMS are affected by mobility (Awokunmi 2015; Yuan et al. 2004). Awokunmi et al. (2015) reported that non-mobile PTMs are distributed in the exchangeable phases of soil. The results in Table 5 revealed the effect of application of saw dust on contaminated soil as there were reduction in percentage of mobile fraction of PTMs as calculated from the Eq. 1 as 3.63%.

$$\text{Average reduction in mobility} = \frac{\textit{sum of mobility of metal in amended soil}}{\textit{number of metals}} \quad (1)$$

However, this form the basis for planning protocols for the field application of saw dust considering the fact that 1 kg of saw dust was added to 4 kg of contaminated soil in pot experimental studies.

The application of amendment (sawdust) to PTMS contaminated soil increased the soil pH as well as the organic matter content of the amended soil due to the presence of high proportion of organic matter. Cation exchange capacity increased upon application of amendment because of the presence of high density negatively charges on the surface of the amendment. These are good indications of positive influence of the amendment on the contaminated soil. Furthermore, the application of amendment to the contaminated soil increased the concentration of the PTMs with higher percentage of the heavy metals either bonded to organic matter or bonded to carbonate, thereby forming a complex with them. Moderate percentages of the PTMs are exchangeable, hence similar to the water extractable proportion. Very low percentage was found as the residual fraction. However, since the application of sawdust as an amendment to the contaminated soil successfully reduced the concentration of

Fig. 1 Sequential extraction of potentially toxic metals in extractive phases of non-amended soil



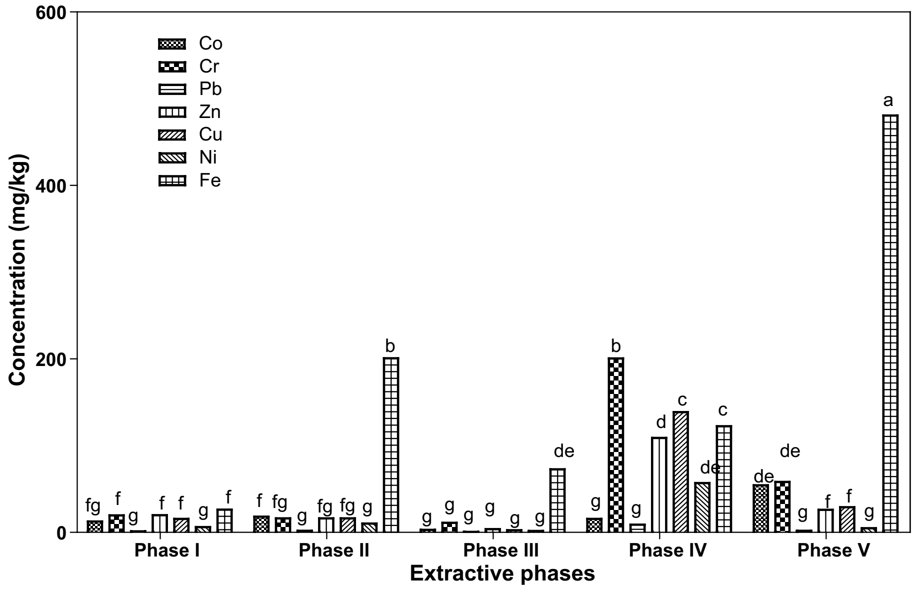


Fig. 2 Sequential extraction of potentially toxic metals in extractive phases of amended soil

Table 5 Percentage mobility of PTMS in amended and non-amended soils

Metals (%)	Co	Cr	Pb	Zn	Cu	Ni	Fe
Non-amended	12.7	14.7	4.6	16.8	16.2	5.6	45.2
Amended	5.5	6.2	2.4	8.7	11.8	3.2	32.4

Cr, Co, Fe appreciably, it can therefore be inferred that this method is effective for the remediation or reclamation of PTMs contaminated soils meant for agricultural purposes especially soils that are heavily contaminated with Cr, Co and Fe.

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