Field Assessment of Progressive Remediation of Soil Contaminated with Lead-Acid Battery Waste in Response to Compost Application

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Abstract

Addition of compost to heavy metal-contaminated soil has been employed to remediate contamination. Such rectification, however, depends on the type of compost and the contaminant involved. The efficacy of Mexican sunflower (MSC) and Cassava peel (CPC) composts applied at 0, 20 and 40 t/ha as well as inorganic fertilizer (NPK, 20:10:10) (100 kg N/ha) on the remediation of a battery waste-contaminated site in Ibadan, Nigeria was assessed. No compost or NPK fertilizer served as the control. The experimental design was a randomized complete block with 4 replicates. Soil analysis before and at 1, 2, 3 and 12 months after compost application was carried out. Mean lead (Pb) concentration (134,000 mg/kg) was high at this site. Twelve months after treatment, MSC and CPC applied at 40 t/ha had reduced the plant available lead concentration in the soil by 69 and 49%, respectively, whereas 20 t/ha had reduced the concentration by 58 and 34%, respectively. The relationships between soil lead and organic matter content ($r = -0.75$), phosphorous ($r = -0.59$) and pH ($r = -0.77$) were negative. NPK fertilizer had a limited effect (7% reduction) on Pb. Application of MSC at 40 t/ha brought about a remarkable reduction in Pb concentration.

1. Introduction

The problem of soil contamination by heavy metals in urban areas has been attributed to the indiscriminate disposal of industrial waste on agricultural land, a practice that poses great risks to the ecosystem and the health of people through contamination of the food chain, air and ground water. The presence of heavy metals on some arable land makes it unsuitable for crop production. Therefore, remediation of such soil is a significant challenge to researchers and government agencies. To date, heavy metal-contaminated sites have been remediated through a relatively narrow range of engineering-based technologies such as excavation, land filling and the use of chemicals. Some of these processes are expensive and require additional site restoration. The selection of treatment, however, takes into account risk assessment before, during and after remediation. In addition, the cost of remediation and the designated use of the land must be considered (Abdel-Sabour *et al.,* 2007). Thus, the development of a cost-effective and environment-friendly method of soil remediation is pertinent.

In recent years, the concept of using compost of high organic matter (OM) content to remediate heavy metal-contaminated sites has attracted a great deal of attention. This is because reducing metal bioavailability and maximizing plant growth through metal inactivation has proved to be an effective method for *in situ* remediation of contaminated sites. *In situ* remediation is much less disruptive to the ecosystem and hydrology, reduces the risk of

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worker exposure during remediation and is typically less expensive than conventional technologies. It also minimizes the mobility of contaminants by transferring them to stable, non-labile phases via chemically and biologically induced transformations (Chaney *et al.,* 1999).

In addition to reducing contaminant levels, compost is known to contain all the essential elements needed for plant growth (Adediran *et al.,* 2003) and reduces the toxic effect of metals on plants (Chaney *et al.,* 1999; Rennevan *et al.,* 2007; Ryan *et al.,* 2007). The potential for compost remediation of metal-contaminated soil by reducing metal leaching and bioavailability has been demonstrated by many researchers (Geebelen *et al.,* 2002; Roman *et al.,* 2003; Castaldi *et al.,* 2005; Simon, 2005; Rennevan *et al.,* 2007; Adejumo *et al.,* 2010). Maximum plant biomass was achieved when minespoil was amended with compost and fertilizer in combination (Nottidge *et al.,* 2005).

Addition of composted sewage sludge to lead (Pb)-contaminated soil was found to bind lead and thus reduce its mobility (Chaney *et al.,* 2000). The higher the insolubility of Pb, the lower its susceptibility to leaching, plant uptake and mammal ingestion. Compost with a high level of phosphorous has also been found to inhibit the uptake of some major metal contaminants such as Pb due to its metal precipitating properties which enable the formation of pyromorphite and chloro-pyromorphite (Chaney *et al.,* 2000), whereas inorganic fertilizer has been reported to increase the acidity of the soil medium which, in turn, might enhance heavy metal solubility (Stefanov *et al.,* 1995).

Little information, however, is available in Nigeria on the use of compost for the remediation of heavy metal-contaminated soil. The aim of this study was to determine the ability of two types of compost and inorganic fertilizer to restore a battery waste-contaminated site for agricultural production.

Materials and methods

Experimental site, preparation of compost and experimental procedure

The abandoned dumpsite of the defunct Exide Battery Manufacturing Company at Ori-ile, Kumapayi village in Ibadan, Oyo State, South Western Nigeria was used for this study. It is located at 7°24.456´N, 4°00.876´E at an elevation of 174 m above sea level and lies within the transitional forest ecosystem of Nigeria. The battery slag waste, illegally dumped on the large expanse of agricultural land in this area several years ago, has made the land agriculturally unproductive.

Mexican sunflower (MSC) and Cassava peels (CPC) were composted separately with poultry manure in a 3:1 ratio for 12 weeks. Representative samples were taken from matured compost and analyzed for chemical properties using a standard method (Table 1). Each compost was applied at 20 and 40 t/ha while inorganic fertilizer (NPK 20:10:10) was applied at 100 kgN/ha (F1). No compost or NPK fertilizer served as the control. Together, there were 6 treatments (MSC_{20}, MSC_{40}, CPC_{20}, CPC_{40}, F1 and Control) which were replicated 4 times in a randomized complete block design. Mapping and demarcation of the site was carefully carried out to ensure minimal disturbance of the soil. Each plot measured 4 x 3 m. The composts were thoroughly mixed with the soil using the broadcasting method and worked into the soil by light hoeing. NPK fertilizer was applied to the plot receiving fertilizer treatment by the line drilling application method.

Data collection and soil chemical analysis

Data on heavy metals and nutrient compositions in the soil were collected at the following sampling time points: before the application of compost (BAC), 1 month (1MACA), 2 months (2MACA), 3 months (3MACA) and 12 months after compost application (12MACA). The United States Department of Agriculture (1972) field sampling

Table 1. Chemical properties of composts used for amendments

Compost type	(%)		Concentration (mg/kg)					cmol/kg
	C	N	P	Ca	Mg	Pb	Zn	K
CPC	4.89	1.93	930	36300	5290	0.20	141	110
MSC	6.94	2.17	2470	37100	12900	0.20	162	61.5

Key: C: carbon; N: Nitrogen; P: Phosphorus; Ca: Calcium; Mg: Magnesium; Pb: Lead; Zn: Zinc; K: Potassium techniques for soil testing were used, and composite samples were taken per treatment at 0–15 cm depth using a soil auger. Samples were thoroughly mixed, air-dried, ground gently in a porcelain mortar and sieved with a 2-mm sieve before taking a representative sample for chemical and physical analysis. Samples were analyzed for pH (H_2O) using a pH meter, and total phosphorous (P; mg/kg) was determined by the Vanado-Molybdate method, and percentage OM by the colorimetric method after dichromic acid digestion (Walkley and Black, 1934). Total environmentally available concentrations (mg/kg) of copper (Cu), zinc (Zn), cadmium (Cd) and lead (Pb) were estimated from the extract after digesting 1 g of soil sample with 10 ml 2 M nitric acid in a water bath (90–100°C) for 2 h using atomic absorption spectrophotometer (Buck Scientific Model, 210 *VGP*, Chicago, Illinois, USA). The method to extract only the maximum contents of potentially plant available metals for plants has been described previously by John (1972), Anderson (1976), Onianwa (2001), Smejkalova *et al.,* (2003) and Ogundiran (2009a). The plant available fraction of heavy metals is assumed to be the most dangerous form of heavy metals in the environment in terms of food chain input (Smejkalova *et al*., 2003); hence, the choice of this extraction method. Ammonium acetate (pH 7) 1 N was used to extract exchangeable bases after shaking for 30 min and cations were determined using a flame photometer (IITA, 1979). Data on the flora density was also collected from each treatment at BAC, 3MACA and 12MACA by enumerating and weighing the vegetation on each plot before uprooting. The uprooted plants were later reincorporated into each plot to maintain soil chemical status. This was carried out at 3MACA and 12MACA.

Data analysis

Collected data were analyzed using ANOVA, and mean values were separated by the Duncan multiple range test. Pearson correlation analysis was used to compare the relationship between heavy metals and other soil nutrients.

2. Results

Changes in soil heavy metals and nutrient concentrations at different sampling time points

Lead and Cadmium : Among the heavy metals, Pb was the most predominant and its initial mean concentration of its bio-available fraction on the site was 134,000 mg/kg. A significant reduction in Pb concentration was recorded in all compost-amended plots in a progressive order except in the soil amended with CPC_{20} where the concentration had increased by 6% at 12MACA compared with the concentration at 3MACA. A remarkable reduction in Pb concentration was observed in the soil treated with MSC_{40} at 12MACA compared with other treatments, and Pb was reduced from a mean concentration of 134,000 mg/kg at BAC to 43,000 mg/kg ($P<0.05$). This was followed by reductions of MSC_{20} (57,000 mg/kg), CPC_{40} (69,000 mg/kg) and CPC_{20} (89,000 mg/kg) after treatment. MSC_{40} reduced the soil Pb level by 11, 47, 57 and 69% at 1MACA, 2MACA, 3MACA and 12MACA, respectively. On the other hand, there was no reduction in Pb concentration of the plots treated with F1 and control except at 12MACA when the concentration reduced to 125,000 mg/kg for both treatments. However, the percentage reductions calculated at 2MACA were higher than those of other time points for all compost treatments (Table 2).

The initial concentration of Cd was high for all treatments before the application of compost with a mean value of 42.0 mg/kg. At 1MACA, however, the concentration started to reduce in all the compost-amended soils after the application of $CPC_{20,}$ $CPC_{40,}$ MSC_{20} and MSC_{40}, which reduced the concentration to 19.0, 37.0, 26.2 and 21.0 mg/kg respectively. A reduction to 26.0 mg/kg was also recorded for the F1 treatment while there was no reduction for the control. Conversely, the Cd concentration in the soil samples taken at 2MACA increased for all treatments, including the control, to more than that at 1MACA, except in the soil treated with MSC_{40} and CPC_{40}. Overall, the application of MSC_{20} and MSC_{40} gave the lowest Cd concentrations at 12MACA while the highest was recorded in the control soil (Table 3).

Zinc and Copper: Initially, the application of compost generally reduced the Zn concentration until 3MACA, with MSC_{20} giving the lowest concentration followed by CPC_{40}, while MSC_{40} and CPC_{20} treatments had the highest Zn concentration. Zn concentration was reduced from 507.2 mg/kg (average) at BAC to 285.0, 295.0, 343.0 and 382.0 mg/kg for $MSC_{20,}$ $CPC_{40,}$ MSC_{40} and CPC_{20},

Table 2. Effects of treatments on Pb concentrations at different sampling time points

Treatments	BAC	1MACA	2MACA	3MACA	12MACA
Control	133,000^{b}	134,000^{a}	137,000^{a}	139,000^{a}	125,000^{a}
MSC20	136,000^{a}	119,000^{b}	75,000^{c}	71,000^{c}	57,000^{d}
MSC40	138,000^{a}	110,000^{d}	71,300^{d}	58,000^{d}	43,000^{e}
CPC20	132,000^{b}	118,000^{b}	95,300^{b}	84,000^{b}	89,000^{b}
CPC40	134,000^{b}	119,000^{b}	91,000^{b}	85,000^{b}	69,000^{c}
F1	132,000^{b}	133,000^{c}	136,000^{a}	139,000^{a}	125,000^{a}

Note: Figures followed by the same letter are not significantly different from each other ($P<0.05$)

Table 3. Effects of treatments on Cd concentrations at different sampling time points

Treatments	BAC	1MACA	2MACA	3MACA	12MACA
Control	41.0^{a}	40.0^{a}	44.0^{a}	36.0^{b}	24.0^{b}
MSC20	42.0^{a}	26.0^{c}	34.0^{b}	12.0^{e}	3.0^{e}
MSC40	45.0^{a}	21.0^{c}	19.0^{d}	20.0^{d}	3.3^{e}
CPC20	38.0^{b}	19.0^{d}	31.0^{b}	24.0^{c}	14.0^{c}
CPC40	43.0^{a}	37.0^{b}	26.0^{c}	34.0^{b}	11.0^{d}
F1	41.0^{a}	26.0^{c}	48.0^{a}	48.0^{a}	34.0^{a}

Note: Figures followed by the same letter are not significantly different from each other ($P<0.05$)

respectively, at 3MACA. The trend, however, changed at 12MACA, and the concentration increased for all treatments including the control. Zinc concentration in the soil treated with MSC$_{40}$, MSC$_{20}$, CPC$_{40}$ and CPC$_{20}$ increased to 500, 800, 700, 900 mg/kg, respectively, at this time point. Furthermore, there was no difference between the Zn concentration (600 mg/kg) in the soil treated with F1 and the control at 12MACA and the previous sampling time points (Table 4).

Copper concentration also decreased after the application of compost. At 3MACA, relative to the values for CPC$_{20}$ and MSC$_{40}$ treatments, the lowest concentrations of Cu (278.0 and 291 mg/kg) were recorded in the soil treated with CPC$_{40}$ and MSC$_{20}$, respectively. At this time point, the highest concentrations were also recorded in the soil treated with inorganic fertilizer and MSC$_{40}$. The value remained constant in the soil amended with MSC$_{20}$ after the initial reduction at 1MACA whereas it increased sharply for the MSC$_{40}$ treatment at 2MACA. There was a consistent reduction in Cu concentration in the soil treated with CPC$_{40}$ until 12MACA. Unlike other treatments (MSC$_{20,}$ MSC$_{40}$ and CPC$_{40}$) at 1MACA, the Cu values for CPC$_{20}$, F1 and the control increased more than the initial values but were later reduced at 2MACA (Table 5).

Organic matter and phosphorous: The addition of compost caused an increase in the OM content of all compost-amended soils. The OM content peaked at 2MACA at which time the soil treated with MSC$_{40}$ had the highest OM content of 7.5%, whereas at 3MACA, there was a general drop in the OM content levels for all compost treatments. An increase, however, was recorded at 12MACA. Of the compost treatments, the soil treated with CPC$_{20}$ had the lowest OM (4.3%). Furthermore, there was no increase in the OM content of the control, and the soil treated with inorganic fertilizer throughout the sampling time points had the lowest OM content (Table 6).

Total P concentration for all treatments before compost application was low but compost amendment of the contaminated soil and F1 treatment increased the soil P concentration at 1MACA compared with the control soil. Phosphorous concentration increased progressively from BAC to 2MACA and the highest concentration (13400 mg/kg) was recorded in the soil treated with MSC$_{40}$ at 2MACA followed by those of the MSC$_{20}$ (7365 mg/kg) and

Table 4. Effects of treatments on Zn concentration (mg/kg) at different sampling time points

Treatments	BAC	1MACA	2MACA	3MACA	12MACA
Control	528^{b}	681^{a}	457^{a}	540^{b}	600^{d}
MSC20	492^{c}	243^{f}	367^{c}	285^{e}	800^{b}
MSC40	571^{a}	410^{d}	412^{b}	343^{d}	500^{e}
CPC20	456^{d}	457^{c}	430^{a}	382^{c}	900^{a}
CPC40	467^{d}	291^{e}	344^{d}	295^{e}	700^{c}
F1	529^{b}	605^{b}	459^{a}	581^{a}	600^{d}

Note: Figures followed by the same letter are not significantly different from each other ($P<0.05$)

Table 5. Effects of treatments on Cu concentration (mg/kg) at different sampling time points

Treatments	BAC	1MACA	2MACA	3MACA	12MACA
Control	431^{e}	574^{a}	329^{d}	329^{c}	472^{a}
MSC20	487^{c}	289^{e}	290^{e}	290^{d}	330^{c}
MSC40	583^{a}	278^{e}	440^{b}	440^{a}	350^{c}
CPC20	484^{c}	410^{c}	375^{c}	375^{b}	480^{a}
CPC40	505^{b}	376^{d}	278^{e}	278^{e}	300^{d}
F1	461^{d}	515^{b}	486^{a}	456^{a}	440^{b}

Note: Figures followed by the same letter are not significantly different from each other ($P<0.05$)

Table 6. Effects of treatments on OM contents (%) of the experimental site at different sampling time points

Treatments	BAC	1MACA	2MACA	3MACA	12MACA
Control	0.8^{a}	1.0^{d}	1.2^{d}	1.1^{d}	1.2^{d}
MSC20	1.0^{a}	6.1^{a}	7.0^{a}	3.6^{a}	4.2^{b}
MSC40	1.2^{a}	6.4^{a}	7.5^{a}	4.9^{a}	5.5^{a}
CPC20	0.6^{a}	2.0^{c}	4.3^{c}	1.8^{c}	2.6^{c}
CPC40	0.6^{a}	3.0^{b}	5.1^{b}	3.1^{b}	4.8^{b}
F1	0.7^{a}	1.0^{d}	1.7^{d}	1.0^{d}	1.3^{d}

Note: Figures followed by the same letter are not significantly different from each other ($P<0.05$)

CPC_{40} (6802 mg/kg) treatments. Similar to what was observed in soil OM, at 3MACA, P level started declining except for CPC_{20} treatments where the value increased from 1525 mg/kg to 2054 mg/kg. These values, however, had decreased at 3MACA to 1012, 823 and 2392 mg/kg for MSC_{40}, MSC_{20} and CPC_{40}, respectively. On the other hand, there was a reduction in the concentration of P in the soil amended with CPC_{20} and CPC_{40} treatments at 12MACA; P increased in the soil treated with MSC_{20} (1200 mg/kg) and MSC_{40} (3600 mg/kg). The control had the lowest P concentration (167 mg/kg; Table 7).

Potassium, Calcium and Nitrogen: The addition of compost generally increased the concentration of the macronutrients in this soil compared with non-amended plots. The K concentration of all compost-treated soils were higher than that of the control, and the highest K level was recorded at 2MACA in soil amended with CPC_{40}, followed by that of MSC_{40} (Table 8). The concentration, however, started to reduce at 3MACA. Calcium concentration increased in line with the increase in compost application rate and was more pronounced in the soil amended with MSC. In contrast, only a slight difference was observed in the Ca concentration of the soil amended with CPC at both rates. Overall, at each sampling time point, the value of Ca recorded for the soil amended with MSC_{40} was the highest, although it started declining from

Table 7. Effects of treatments on P concentrations in mg/kg at different sampling time points

Treatment	BAC	1MACA	2MACA	3MACA	12MACA
Control	145^{c}	165^{f}	201^{f}	150^{f}	167^{e}
MSC20	138^{d}	899^{e}	7365^{b}	823^{d}	1200^{c}
MSC40	165^{b}	11556^{a}	13390^{a}	1012^{c}	3600^{a}
CPC20	175^{b}	3134^{c}	1525^{d}	2054^{b}	1500^{b}
CPC40	135^{d}	5075^{b}	6802^{c}	2392^{a}	1600^{b}
F1	187^{a}	1224^{d}	725^{e}	750^{e}	860^{d}

Note: Figures followed by the same letter are not significantly different from each other ($P<0.05$)

Table 8. Effects of treatments on K concentrations (cmol/kg) at different sampling time points

Treatments	BAC	1MACA	2MACA	3MACA	12MACA
Control	0.6^{a}	1.3^{e}	0.8^{e}	0.9^{c}	0.7^{b}
MSC20	1.2^{a}	6.1^{b}	7.1^{b}	1.7^{a}	1.3^{b}
MSC40	0.7^{a}	6.2^{b}	2.7^{c}	1.2^{c}	1.1^{b}
CPC20	1.0^{a}	4.2^{c}	2.8^{c}	1.2^{c}	1.6^{a}
CPC40	0.8^{a}	10.2^{a}	13.3^{a}	1.5^{b}	1.1^{b}
F1	0.6^{a}	2.7^{d}	1.6^{d}	1.5^{b}	1.2^{b}

Note: Figures followed by the same letter are not significantly different from each other ($P<0.05$)

Table 9. Effects of treatments on Ca(mg/kg) concentrations at different sampling time points

Treatments	BAC	1MACA	2MACA	3MACA	12MACA
Control	244^{b}	242^{e}	246^{d}	244^{e}	232^{e}
MSW20	244^{b}	1280^{c}	1320^{b}	1280^{d}	1380^{c}
MSW40	254^{a}	5400^{a}	4440^{a}	3450^{a}	2500^{a}
CPW20	260^{a}	1200^{d}	1300^{b}	1550^{b}	1370^{c}
CPW40	234^{b}	1350^{b}	1250^{c}	1450^{c}	1570^{b}
F1	244^{b}	230^{e}	250^{d}	258^{e}	251^{d}

Note: Figures followed by the same letter are not significantly different from each other ($P<0.05$)

2MACA (Table 9).

Nitrogen (N) determination was carried out only at BAC, 2MACA and 12MACA. Nitrogen concentration responded positively to compost addition and inorganic fertilizer. Soil amended with MSC$_{40}$, followed by CPC$_{40}$ and MSC$_{20}$, had the highest value of N at 2MACA and was followed by treatments of CPC$_{40}$ and MSC$_{20}$. At 12MACA, the concentration reduced for MSC$_{20}$, MSC$_{40}$, CPC$_{40}$ and F1 treatments but increased for CPC$_{20}$ (Table 10).

Table 10. Effects of treatments on N(%) concentrations at different sampling time points

Treatments	BAC	3MACA	12MACA
Control	0.2^{a}	0.1^{b}	0.1^{a}
MSC20	0.1^{a}	0.3^{b}	0.2^{a}
MSC40	0.1^{a}	0.6^{a}	0.2^{a}
CPC20	0.3^{a}	0.2^{b}	0.2^{a}
CPC40	0.1^{a}	0.3^{b}	0.2^{a}
F1	0.1^{a}	0.2^{b}	0.1^{a}

Note: Figures followed by the same letter are not significantly different from each other ($P<0.05$)

Pearson correlation between heavy metals, pH and other soil nutrients

Results of the correlation analysis revealed that the OM content was inversely and significantly correlated with the concentration of all heavy metals (except Zn) in the

Table 11. Pearson correlation between heavy metals and other soil nutrients

	pH	Mg (mg/kg)	K (cmol/kg)	Om (%)	Ca (mg/kg)	P (mg/kg)
Pb (mg/kg)	-0.8***	-0.5*	-0.1ns	-0.8***	-0.4ns	-0.6***
Cd (mg/kg)	-0.7**	-0.5*	0.1ns	-0.6**	-0.3ns	-0.6**
Cr (mg/kg)	-0.8***	-0.4ns	-0.14ns	-0.7**	-0.3ns	-0.5**
Zn (mg/kg)	-0.5*	-0.3ns	0.1ns	-0.4ns	-0.3ns	-0.5*
Cu (mg/kg)	-0.8***	-0.4ns	-0.2ns	-0.7**	-0.2ns	-0.2ns

* = Correlation was significant at P=0.05
*** = Correlation was significant at P=0.01
Ns = Not significant

soil. The same trend was observed for soil pH ($p<0.05$). An inverse correlation indicates that an increase in soil OM content caused a reduction in the heavy metal concentration of the contaminated soil. Likewise, an increase in soil pH results in a lower concentration of heavy metals in the soil.

The magnesium (Mg) concentration in the soil was also inversely correlated with soil Pb and Cd concentrations, but its correlation with Zn and Cu was not significant, even though it was inverse. Except for that of Cu, the correlation between soil P and other heavy metals were significant and inverse while that of Ca, though inverse, was not significant. These relationships mean that a high P concentration reduces the heavy metal concentration while a Ca concentration has no significant effect. Soil K concentration showed no correlation with soil heavy metal concentrations (Table 11).

Re-establishment of vegetation

Before compost application, there was no significant difference between the plots with regards to vegetation density, which was low. After the application of compost, the enumeration of flora density carried out at 3MACA showed that compost application had a significant ($P<0.05$) effect on vegetation re-establishment. Compost amendment stimulated the emergence of vegetation more than inorganic fertilizer and produced the highest flora density. Compost also had a significant effect on vegetation density at 12MACA, and the density at this time point was superior to that at 3MACA. However, of the two compost types, MSC enhanced vegetation re-establishment more than CPC. Unlike the observations at 3MACA, the application rate of 40 t/ha gave the highest quantity of vegetation which was significantly higher than that of 20 t/ha. The plots treated with inorganic fertilizer also produced the highest quantity of vegetation compared with the control plots but not with the compost-amended plots (Fig. 1).

3. Discussion

The concentration of the initial environmentally

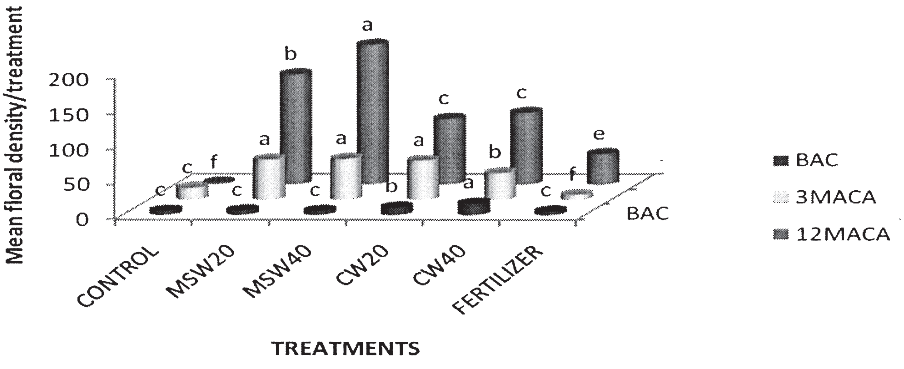

Fig. 1. Effects of treatments on floral density at different sampling time points

available Pb on the site exceeded the European Union maximum permissible values for agricultural soils (50–300 mg/kg for Pb; Council of the European Communities, 1986; Kabata-Pendias and Pendias, 2001). The results of the present study confirmed the findings of Ogundiran (2007) while working on the open battery waste dumpsite and can be attributed to the fact that the main components of lead-acid batteries include lead and its oxides (Oldema, 1994; Birkefield *et al.,* 2007; Osibanjo, 2008). Initial variation observed in the chemical properties of the soil before application of compost could be due to the non-homogeneity of the site since soil samples were taken separately from each plot depending on the treatment allocation coupled with the fact that the samples were analyzed separately.

The general reduction in soil Pb concentration in all compost-amended plots observed in this study could be due to the transformation of available soil Pb into stable, non-labile phases via chemically and biologically induced transformations (Chaney *et al*., 1999). Chemical transformation of soil Pb (plant available form) into stable lead pyromorphites in the presence of Ca- and P-containing chemicals/amenders has been reported (Melamed *et al.,* 2003; Chaney *et al*., 1999; Chaney *et al*., 2000; Ogundiran and Osibanjo, 2009a). Therefore, it would not be out of place to propose that chemical reactions occurred between the contaminated soil, which contained high levels of Ca and P, and the composts used for amendment (Table 1). Calcium ions in the compost probably exchanged with the Pb ions in the contaminated soil and subsequently reacted with the phosphate in the compost as demonstrated by the following equation (Ogundiran, 2007):

$$\text{Ca, H, PO}_4\text{ (compost)} + \text{H}_2\text{O (l)} \overset{\text{dissolution}}{\rightleftharpoons} \text{Ca}^{2+}\text{ (aq)} + \text{H}_2\text{PO}_4^{-}\text{ (aq)} + \text{OH}^{-}\text{ (aq)}$$

(Calcium hydrogen phosphate)

$$5\text{Pb}^{2+}\text{(aq)} + 3\text{H}_2\text{PO}_4^{-}\text{ (aq)} + \text{H}_2\text{O (l)} \overset{\text{pyromorphite formation}}{\rightleftharpoons} [\text{Pb}_5\text{ (PO}_4)_3\text{OH] (s)} + 7\text{H}^{+}\text{ (aq)}$$

(Soil Pb) (pyromorphite)

In addition, chemical transformation of Pb in the compost-amended soils might also be attributed to the reaction of the former with humic and fulvic acids in the latter. A previous report by Rennevan *et al*., (2007) supports this possibility. Humic material has been reported to have functional groups that are capable of acting as ligands for the formation of insoluble complexes with heavy metals (Brown *et al.,* 2009). Divalent transition metal ions such as Pb^{2+} and Cu^{2+} are known to bond covalently with humic acid more than alkaline earth metal ions (Ca^{2+} and Mg^{2+}) because the latter cannot bond covalently (Gary and Stephen, 2000). Strong covalent bonding resulting in the formation of a stable six-membered chelate between the salicylate functional group of humic acid and Pb^{2+} has been reported to be a particularly important reaction for Pb complexation in Pb-contaminated soil amended with compost (Gary and Stephen, 2000). The stability constant for this reaction, which has been determined as 10^6, might have contributed to the complex stability resulting in the immobilization of Pb in the soil matrix. Humic acid has also been reported to precipitate metals in solution (Lindsay, 1979), thereby increasing adsorption (Jahiruddin *et al.*, 1985) and thus lowering the amount in the plant available and ecologically significant fractions. Humic acid also increases its concentration in other stable and insoluble fractions (Shuman, 1998; Rennevan *et al.*, 2007) that cannot be destroyed by the digestion method used in this study (Amacher, 1996; Smejkalova *et al.*, 2003). According to Amacher (1996), the method that can destroy other stable fractions, in particular the resistant silicate minerals, and give a more complete digestion and sample dissolution must include hydrofluoric acid in the digestion sequence, as described by Baker and Amacher (1982).

Furthermore, it has been reported that the plant available fraction of metals may be reduced through binding to nutrient anions in compost-amended plots (Timothy *et al*., 2001). The immobilization of Pb was reported to be well-correlated with soil cation exchange capacity and pH, thereby resulting in increased metal adsorption (Shuman, 1998). The increase in soil pH (data not shown) as a result of compost addition was probably responsible for the lower concentrations of heavy metals recorded in compost-amended soil by reducing their solubility which in turn reduced metal uptake by plants, as reported by Adejumo *et al.,* (2010) on maize planted on compost-amended contaminated soils. Accumulation of Pb in maize tissue was reduced due to Pb immobilization in the amended plots when compared with controls. A higher application rate increased the soil pH more than a lower rate and consequently might be the reason for the significant reduction in heavy metal concentration in the soil amended by application of 40 t/ha (McBride, 1994; Ryan *et al*., 2007).

The significant reduction in Pb concentration observed at 2MACA in compost-amended plots could be attributed to the increase in the OM content, which was also at its peak at this time point, while the observed reduction in the OM content at 3MACA was probably the result of the biodegradation of OM. Consequently, the increase in soil nutrient and OM due to plant decay could have contributed to the increased rate of heavy metal reduction at 12MACA. The increase, but not decrease, in Pb concentration in inorganic fertilizer treatment at 2MACA confirms the report of Stefanov *et al.,* (1995) and can be attributed to the increased acidity of the soil medium arising from application of inorganic fertilizer which in turn enhances heavy metal solubility. The increase in soil acidity could have aided the dissolution of heavy metals in this treatment and that of the control as they have been reported to become more soluble in an acidic environment. However, the reduction observed in the heavy metal concentrations of the control and soil treated with inorganic fertilizer at 12MACA could be due to the run-off from compost-treated plots to untreated plots.

A higher application rate of compost was found to be more effective probably due to the fact that the nutrient ions at this rate were higher than those at a lower rate and thereby suppressed the heavy metal ions (Greger *et al*., 1991; Timothy *et al*., 2001). The higher rate also increased the concentrations of Ca, P and K in the compost-amended soil and might be responsible for the strong negative correlation that exists between heavy metals and essential macro-elements. The negative correlation between soil OM content and heavy metals seems to confirm the reports of previous research (Tsadilas *et al*., 1995; Shuman, 1998) and is presumably due to the formation of insoluble complexes between heavy metals and OM content. Reduction in the concentrations of all the soil nutrients and OM content at 3MACA could be attributed to the breakdown and subsequent uptake by the plants that emerged on the compost-amended plots. These findings are in agreement with those reported by other researchers (Pier *et al*., 1992; Clemente *et al*., 2006). The increase in the Zn concentration starting from 3MACA, although within the acceptable range of 1-1500 mg/kg (Kabata-Pendias and Pendias, 2001), could be attributed to compost amendments since Zn is one of the micronutrients required for plant growth and can be supplied by adding compost to the soil (Adediran *et al.*, 2003). The P and K concentrations that were higher in the soil treated with NPK than in the control were due to the presence of these elements in the applied inorganic fertilizer. Flora density was enhanced on all compost-amended plots due to the ability of compost to supply the soil with the essential nutrients needed for the plant growth and the reduction in the form of heavy metals available to the plants (Togun *et al*., 2003; Rennevan *et al*., 2007). These results are also in agreement with the finding of Ryan *et al.,* (2007) wherein organic amendment decreased the toxic plant available heavy metal concentrations thereby promoting plant growth.

4. Conclusion

The present study showed that Pb was prevalent in the battery waste dumpsite. However, the application of compost was effective in reducing the plant bio-available heavy metal concentrations in the contaminated soil. Such remediation has the potential to reduce the attendant health risk through the food chain which is generally associated with heavy metal-contaminated soils. The effectiveness of compost, however, varied based on plant materials and the rate of application. The higher the rate of application, the more effective the compost. Compost prepared from Mexican sunflower was more effective than that of cassava peels. Irrespective of the sampling time point, the results showed that MSC_{40} reduced the concentrations of Pb, Cu and Cd more than the other treatments. It also supplied the soil with more of P, Ca and OM. The addition of inorganic fertilizer did not cause a Pb reduction in the soil. A positive but strong inverse correlation was established between Pb concentration and OM content in the soil. However, the fate of heavy metal which is assumed to have been bound in the organic fraction still needs to be investigated further. The immobilized form may become plant available over time. There is a need therefore for repeated use of compost to reduce Pb concentration in the soil to a safe level and ensure continuous binding in non-labile forms before cropping.

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