



Soil amendment with compost and crop growth stages influenced heavy metal uptake and distribution in maize crop grown on lead-acid battery waste contaminated soil

Sifau A. Adejumo^{a,*}, Mary B. Ogundiran^b, Adeniyi O. Togun^a

^a Department of Crop Protection and Environmental Biology, University of Ibadan, Ibadan, Oyo State, Nigeria

^b Analytical chemistry/Environmental Unit, Department of Chemistry, Faculty of Science, University of Ibadan, Nigeria



ARTICLE INFO

Keywords:

Organic amendment
Immobilization
Metals
Remediation
Plant age

ABSTRACT

Heavy metal contamination of agricultural soils poses serious risk to human health through food chain. Immobilization technique to reduce metal bioaccumulation in plant tissues is being promoted. Field experiment was carried out on heavy metal contaminated site to test for the efficacy of different organic amendments (Mexican sunflower compost (MSC) and Cassava peel compost (CPC) applied at 0, 20 and 40 t/ha) and inorganic fertilizer (NPK; 20:10:10 at 100 kg Nitrogen /ha) in metal immobilization and uptake by maize crop at different growing stages (one, two month(s) after planting (1MAP, 2MAP) and at harvesting). Compost amendments generally reduced heavy metal accumulation in maize crop unlike NPK and control where high metal toxicity led to plant death at 2MAP. Pb was highly accumulated at every growing stage followed by Cd while Cr concentration was below the detection limit at harvesting. Bioaccumulation and transfer factors were found to depend on maize growing stage with higher accumulation at 1MAP. Percentage Pb accumulation in the shoot was more at 1MAP but reversed at 2MAP and harvesting with higher accumulation in the root. Application of MSC and CPC at 20 and 40 t/ha reduced Pb accumulation in maize by 37.8–64.7% compared with control and the reduction at harvesting was more significant than those recorded at 1MAP and 2MAP. The study concluded that compost reduced heavy metals accumulation in maize crop and that metal accumulation depends on maize growth stage.

1. Introduction

Most agricultural lands have been contaminated with heavy metals from different anthropogenic sources such as industrial activities, agricultural practices, smelting, mining operations and the use of municipal wastewater for agricultural production [1,2]. The most blamed source of land contamination is through the indiscriminate disposal of industrial wastes [3]. Typical examples of such land are as found in Ibadan Metropolis, Nigeria where several hectares of agricultural land in about five villages (Lalupon, Kumapayi, Erunmu, Ile-igbon and Olodo) have been contaminated by high levels of heavy metals as a result of indiscriminate disposal of lead-acid battery wastes [1,4]. Excessive heavy metal accumulation in agricultural soils and the consequent accumulation in crops pose serious risk to human health through food chain. [5–7]. Pb is neurotoxic and carcinogenic to both animal and human being [5,6]. The recent advocate on increasing agricultural production to meet the food needs of the ever increasing

population most especially in developing countries, through expansion of arable lands and the practice of urban agriculture necessitate the need to convert most contaminated and abandoned land areas to arable lands. Thus, the development of a cost-effective and environment-friendly method of soil remediation to increase the amount of cultivable land and reduce/prevent heavy metal accumulation in food crop is therefore pertinent for increasing agricultural production.

Heavy metals, unlike organic contaminants are not easily degradable. The most preferred remediation technology commonly used for heavy metals contaminated soil is immobilization to decrease their labile fractions in the soil and minimize uptake by plants [4,8–13]. This, unlike other remediation techniques such as land-filling, excavation, chemo-remediation, soil washing and flushing has been reported to be cost effective, accessible and environment-friendly. To achieve metal immobilization, soil amendment with different organic materials in the form compost to increase soil fertility and pH levels which in turn reduce metal bioavailability has been widely reported [9,11–16]. It has

* Corresponding author.

E-mail address: nikade_05@yahoo.com (S.A. Adejumo).

been found to reduce the toxic effects of heavy metals in crop, improve the fertility of contaminated soil, reduce the bioavailability and leachability of heavy metals through increased soil pH and modify plant nutrition by increasing the amount of nutrient ions over the heavy metal ions [4,8–1012,13].

The benefits and efficacy of compost in remediation however depend on the type of organic matrices, source, compost maturity, rate of application, types and concentrations of heavy metals, [16–18]. Effectiveness of any immobilizing agent is also based on its ability to permanently keep the metal in bound form and prevent its uptake by plant [12]. Some authors reported that the adsorbed metals in compost amended contaminated soil might be made available for plant uptake in the long run [18,19]. There is need, therefore, to assess the effectiveness of compost in reducing metal bioavailability for uptake by plant and keeping the metals in bound form throughout the cropping season. The plant growing stage at which metal immobilization is more effective and metal uptake is minimal must also be determined. This will help in determining the suitability of compost amended contaminated soil for crop production and the end-use or fate of the crop grown on contaminated soil most especially food crop.

The experiment was carried out to (a) assess the effectiveness of different compost amendments and inorganic fertilizer in immobilizing heavy metals (lead, Cadmium and Chromium) in contaminated soil thereby reducing plant uptake, (b) determine the relationship between plant growing stages and metal accumulation or uptake by plant and (c) investigate the mobility of these metals and accumulation in the above – ground parts in response to different amendments and plant growing stages. Maize crop (*Zea mays L.*) which is a staple food crop and is popularly cultivated most especially in the study area was used as a test crop. The major goal was to ensure that the levels of heavy metals in agricultural crops remain sufficiently low so as to reduce the risk of food contamination and avoid adverse effects on human health. The findings of this study will be a useful guide in assessing the risk associated with the use of contaminated soil for agricultural purposes and the ameliorative effects of organic amendments on crop grown on metal contaminated site. It will also provide a way of remediating contaminated agricultural land thereby expanding the amount of cultivable lands.

2. Materials and methods

2.1. Description of the experimental site

The experiment was carried out on one of the abandoned lead-acid battery wastes polluted sites located at Ori-ile, Kumapayi village of Egbeda Local Government area (near Ibadan), Oyo State, Nigeria where battery slag wastes were illegally dumped on a large expanse of agricultural land by the defunct West Africa Battery Manufacturing Company several years ago. The study site is located at longitude 7° 24', N latitude 4° 00'E and an elevation of 174 m above sea level. Lead (Pb) was most predominant in this soil being the major constituent of lead acid battery with total concentration of 138,000 mg/kg. Chromium (Cr; 12.3 mg/kg), Cadmium (Cd; 41.3 mg/kg), Copper (Cu; 482 mg/kg) and Zinc (Zn; 1510 mg/kg) were also present. The concentrations of these five metals were high compared to the permissible levels recommended by [20,21] in soils (Table 1) but Pb which was highly concentrated in this soil was mostly focused on as well as Cd and Cr. The soil was acidic with low pH (water soil = 2.5:1) value of 4.2 and poor in soil nutrients (OC: 1.24%, N: 0.12%, P: 125 mg/kg, Ca: 171.20 mg l/kg, Mg: 23.04 mg/kg). The soil is classified as clay soil and made up of 36, 49 and 14% sand, clay and silt respectively [22]. The presence of these battery slag wastes on the land had rendered it infertile and brought a lot of hardship to people living in this area as the affected community has reportedly had cases of crop failure, livestock death and several unexplainable diseases due to the pollution of the environment [23]. According to the residents, this contaminated site used to be an

Table 1

Guidelines for safe limits of heavy metals in soil and plants.

Source: Singh et al. [7].

Samples	Source	Cd	Cu	Pb (µg/g)	Zn	Cr
Soil	WHO/FAO [36]	–	–	–	–	–
	European Union Standards [20]	3.0	140	300	300	150
Plant	WHO/FAO [36]	0.2	40.0	50	60.0	–
	European Union Standards [21]	0.2	–	0.30	–	–

agricultural land before the indiscriminate dumping of the wastes by the company. The results of the preliminary experiment in the greenhouse with this soil showed that this soil can be used for cropping if amended with compost [24]. This prompted our selection of one of these contaminated sites for field study.

2.2. Compost preparation and experimental procedure

Composts were prepared by mixing Mexican sunflower (MSC) and cassava peels (CPC) separately with poultry manure at the ratio of 3:1 and composted for 12 weeks as described by Adediran et al. [17]. The choice of the composts and rates was based on the preliminary experiments carried out on this soil where eight types of organic materials were screened. The chemical composition of each compost [16] is shown in Table 2. Both were applied at the rates of 0, 20 and 40 t/ha while inorganic fertilizer (NPK, 20:10:10) which is commonly used by farmers in this region was applied at recommended rate of 100 kg Nitrogen / ha and denoted as F1 [25]. The plots without compost amendment and inorganic fertilizer (NPK 20:10:10) served as control. The treatments were designated as MSC40, MSC20, CPC40, CPC20, F1, and Control. The six treatments were replicated four times in a randomized complete block design to give four blocks. Compost application was carried out one month before maize planting to give sufficient time for proper equilibration to avoid nutrient confliction between plant and micro-organisms. The composts were applied on the soil surface and then mixed thoroughly up to 5 cm by light hoeing. Inorganic fertilizer was applied two weeks after planting using line application method. Maize seeds (SWAM Y-X2 variety) which were obtained from the Institute of Agricultural Research and Training, Moor Plantation, Ibadan, Nigeria were used. The spacing for maize planting was 75 cm between and 25 cm within rows. Manual weeding was carried out to suppress and control weed intervention.

2.3. Data collection

Data were collected on total soil heavy metal concentration before and at one month intervals, metal concentration in different fractions in soil, metal concentration in different plant parts at each sampling period, Bioaccumulation and translocation factors,

2.3.1. Sequential extraction or heavy metal fractionation

Before application of compost and after site demarcation, soil samples were taken from each plot for the determination of heavy metal

Table 2

Chemical properties of composts used for amendments.

Source: Adejumo et al. [16].

Compost Type	C (%)	N (%)	P (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	K (cmol/kg)
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

CPC: Cassava Peels Compost, MSC: Mexican Sunflower Compost.

concentrations in the exchangeable and organically bound fractions. The soils were mixed together, air-dried, crushed and sieved through 2 mm and 0.5 mm meshes and composite sample taken for chemical analysis. The sequential extraction was also repeated after harvesting. Heavy metal fractionation is usually into six operationally defined fractions; water soluble (F1), exchangeable (F2), carbonate bound (F3), Fe-Mn oxides bound (F4), organically bound (F5) and the residual form (F6) [77]. For the purpose of this study, since the interest was on the determination of the metals in available/exchangeable and organically bound forms, the method used only focused on exchangeable and organically bound fractions. The method described by Amacher [26] and which had been used by many authors [75] and [27] was used in this experiments. Water extractable plus exchangeable fraction was extracted with 0.1 M $\text{Ca}(\text{NO}_3)_2$ by putting 0.5 g of already sieved and prepared soil sample in a 50 ml graduated plastic centrifuge tube. 10 ml of 0.1 M $\text{Ca}(\text{NO}_3)_2$ was then added, shook for 2 h at 180 cycles per minute in a reciprocating shaker for proper mixing of soil components with the solution and centrifuged at 1500 rpm for 10 min. The supernatant was then decanted and filtered to remove the floating organic matter and retained for analysis. The residue was washed 3 times with 5 ml ethanol and centrifuged each time for five minutes to separate the residue. The ethanol was discarded and the residue was evaporated to dryness.

For organic matter phase, 10 ml of pH 8.5, 5.25% NaOCl solution was added to the residue from previous stage to selectively oxidize organic matter without causing any damage to carbonate, metal oxides and silicate clay phases in the soil [28,29]. The resultant mixture was then mixed thoroughly and placed in a boiling water bath for 15 min. After cooling, it was centrifuged for 10 min. at 1500 rpm and the supernatant decanted into evaporating dish. The sodium hypochlorite treatment was repeated until the organic matter was destroyed as signified by the appearance of pink colour (permanganate ion) in the supernatant [30]. The supernatant was added to the evaporating dish after each treatment. The residue was then washed three times with 5 ml of pH 5, 1 M NaOAc to remove the metal especially Pb that was released during the oxidation of organic matter which might have been reabsorbed by the inorganic phases as suggested by Shuman [31]. The supernatant was also added each time to the evaporating dish. The NaOCl solution in the evaporating dish was evaporated to dryness and the residue dissolved in 1:10 HNO_3 . The solution was quantitatively transferred with rinsing to a 25 ml volumetric flask, diluted to volume and analyzed for heavy metals.

2.3.2. Plant tissue analysis

To determine the crop growing stage at which heavy metal uptake is maximal or minimal and evaluate the ability of compost in keeping the metals in bound form throughout the cropping period, maize plants were uprooted and partitioned at one and two months after planting (1MAP, 2MAP) and at harvesting for chemical analysis. At each sampling period, destructive sampling involving two plants from each row on each plot was employed. The plants were carefully uprooted, the roots were gently washed to remove the attached soil and avoid any surface deposits. They were then separated into different parts (i.e., root, leaf, stem, at 1MAP and the post-tasselling partitioning of plant was into root, shoot, spikelets, cobs and grains.) and taken to the laboratory within one hour of harvesting. In the laboratory, the plant parts were bagged separately in paper envelopes and oven-dried to a constant weight at 80 °C. The oven dried samples were ground in a Wiley mill and processed for the determination of Pb, Cd and Cr concentrations in the plant tissue using dry ash method as described by Ogundiran [32]. The milled samples of 1 g were weighed into porcelain crucibles and ashed at 450 °C for 6 h. The resultant ash contents were re-dissolved in 10 ml of 2 M HNO_3 , heated on the hot plate, sieved into 25 ml volumetric flask and made up to the mark. The filtrates were then analyzed for heavy metals using Atomic Absorption Spectrophotometer (210 VGF, Buck Scientific, Chicago, Illinois) of air acetylene gas. The

plant tissue analyses were determined for the maize crop from all the treatments including control at 1MAP and 2MAP while it was only determined in compost treatments at harvesting due to the death of maize crops in control and F1 treatments between 2MAP and harvesting.

2.3.3. Determination of transfer, translocation and bioaccumulation factors

Transfer factor (TF) to the leaf at 1 MAP, 2 MAP and seed at harvesting) was determined for every element using the formula described by Singh et al. [7] and expressed in percentage (i.e $\text{TF} (\%) = \text{concentration of metal in edible part} / \text{concentration of metal in soil} \times 100$). The distribution ratio of Pb in the root and shoot at each growing stage in relation to dry matter accumulation was also calculated to determine the effectiveness of compost and inorganic fertilizer on immobilization and upward movement of Pb in maize plant tissue by using the formula;

Distribution ratio of Pb in the shoot = $(\text{Pb concentration in stem} \times \text{stem dry weight} + \text{Pb concentration in leaf} \times \text{leaf dry weight}) / (\text{Pb concentration in the stem} \times \text{stem biomass} + \text{Pb concentration in leaf} \times \text{leaf biomass} + \text{Pb concentration in root} \times \text{root biomass}) \times 100$.
Distribution ratio of Pb in the root = $100 - \text{Distribution ratio of Pb in the shoot}$ or $\text{Pb concentration in root} \times \text{root biomass} / (\text{Pb concentration in the stem} \times \text{stem biomass} + \text{Pb concentration in leaf} \times \text{leaf biomass} + \text{Pb concentration in root} \times \text{root biomass}) \times 100$

The Translocation Factor (TIF) for metals within a plant was determined to evaluate the extent of metal translocation from roots to shoots. It was calculated as the ratio of Metal in the Shoot / Metal in the root. Similarly, Bioaccumulation Factor (BAF) to determine the ability of organic amendments and inorganic fertilizer in immobilizing metal in the soil and reducing its accumulation by plant was calculated for the shoot and root as the ratio of metal in the plant part on dry weight basis and that of the soil (Metal concentration in the plant part / Metal concentration in the soil) as described by Ghosh and Singh [33] and adopted by Singh et al. [34]. The relationship between Pb concentrations in the plant and the soil organic matter content was also determined using correlation coefficient.

2.4. Statistical analysis

This was performed using SYSTAT 11.0 (2008; Systat Software, Inc., Chicago, IL, USA). Differences in heavy metal concentrations among treatments (MSC40, MSC20, CPC40, CPC20, F1, and Control), maize parts (leaf, stem, and root), and time (1MAP, 2MAP, and harvest time) were tested using one-way ANOVA, respectively. When a significant difference was detected, then a post-hoc test was carried out using the Tukey HSD test. Significance was defined as $P < 0.05$ for all tests.

3. Results

3.1. Effects of different rates of composts and inorganic fertilizer on Pb concentrations in maize at different growth stages

Table 3 shows that, lead (Pb) concentrations in maize crop at every growing stage, were significantly reduced with addition of compost compared to control. At each sampling period, application of compost reduced Pb concentrations in all the plant parts compared to inorganic fertilizer with higher compost rate performing better than lower rate. We found more clear effects of plant growing stage and compost application on Pb concentrations in maize crop at every sampling stage. At one and two month(s) after planting, the highest concentrations of Pb were recorded in the maize plants that received inorganic fertilizer treatment and control. Higher amount of Pb was also recorded in all the treatments at 1MAP compared to 2MAP. There was significant difference in the total Pb concentrations in the maize crop sampled at 1MAP and other sampling periods. Put together, the total Pb concentrations in maize plant tissue at 1MAP was higher than those of 2MAP and

Table 3
Effects of treatments on Pb concentrations and distribution in maize plant parts at 1MAP, 2MAP and harvesting.

Treatments	1MAP			2MAP				Harvesting					
	Root mg kg ⁻¹	Stem	Leaf	Root mg kg ⁻¹	Stem	Leaf	Spikelet	Root mg kg ⁻¹	Stem	Leaf	Sheath	Cob	Seed
Control	17000 ^{aAα}	6790 ^{cBβ}	11800 ^{aBα}	15900 ^{aAα}	6920 ^{bBα}	6810 ^{aCβ}	NA	NA	NA	NA	NA	NA	NA
MSC20	9670 ^{bAβ}	3680 ^{dCα}	8790 ^{bBα}	9060 ^{bAγ}	562 ^{cCβ}	591 ^{bBβ}	590 ^{bB}	11200 ^{abAα}	178 ^{cdBγ}	165 ^{abCγ}	110 ^{abE}	58.5 ^{aF}	152 ^{cD}
MSC40	9940 ^{bAβ}	8410 ^{abBα}	8390 ^{bCα}	9270 ^{bAγ}	474 ^{cBβ}	472 ^{bbγ}	231 ^{cC}	13400 ^{aAα}	334 ^{bcCγ}	530 ^{abβ}	222 ^{abD}	50.6 ^{aF}	174 ^{bcE}
CPC20	9750 ^{bAβ}	7560 ^{bcCα}	9130 ^{abBα}	11000 ^{bAα}	809 ^{cCβ}	992 ^{bbβ}	370 ^{cD}	11400 ^{abAα}	430 ^{bbγ}	204 ^{abEγ}	272 ^{abD}	38.5 ^{bF}	338 ^{aC}
CPC40	9610 ^{bAβ}	3720 ^{dCα}	9090 ^{abBα}	11600 ^{bAα}	524 ^{cdγ}	3420 ^{abβ}	830 ^{Ac}	8700 ^{bAγ}	1179 ^{abβ}	182 ^{bdγ}	304 ^{aC}	52.0 ^{aE}	294 ^{bcD}
F1	17900 ^{aAα}	9070 ^{aCα}	12000 ^{abα}	15780 ^{aAβ}	7930 ^{abβ}	6200 ^{aCβ}	NA	NA	NA	NA	NA	NA	NA

Means followed by the same letter in a column or row are not significantly different from each other ($P > 0.05$).

a, b, c, d, e, f were used to show the significant differences in Pb concentration among the treatments for each plant part at each sampling period.

A, B, C, D, E, F were used to show the significant differences in Pb concentration among the plant parts for each treatment and month.

α β γ were used to show the significant differences in Pb concentration in each plant part at different sampling period.

MSC20 = Mexican sunflower compost at 20 t/ha.

MSC40 = Mexican sunflower compost at 40 t/ha.

CPC20 = Cassava waste compost at 20 t/ha.

CPC40 = Cassava waste compost at 40 t/ha.

F1 = Inorganic fertilizer.

NA: Not available.

harvesting in all the treatments At harvesting, as mentioned earlier, the total Pb uptake by maize was only considered for the maize crops from compost treated plots because those in the control and inorganic fertilizer treated plots had already been uprooted at 2MAP when they started dying. The reduction in all the compost treatments was progressive (i.e 1MAP > 2MAP > Harvesting) and more pronounced at harvesting compared to other sampling periods. Pb concentration was also in the order of Root > Leaf > Stem > Sheath > Seeds > Cob at this period. The amounts of Pb in the maize seeds from treatments: MSC20 (152 mg/kg) and MSC40 (174 mg/kg), were significantly lower than those of CPC40 (294 mg/kg) and CPC20 (338 mg/kg), the latter of which was the highest. Conversely, root Pb concentration in MSC40 was higher than other compost treatments at harvesting. Plant growing stage influenced significantly the distribution and accumulation of Pb in different parts of maize crop. Leaf Pb concentration was more at 1MAP than 2MAP and Harvesting. Similarly, the concentration in the stem at 1MAP was more than those of 2MAP and Harvesting in all the treatments except in control where the concentration at 1MAP was less than that of 2MAP. However, the root Pb concentrations in all the compost treatments at harvesting were the highest except in CPC40 treatment compared to 1MAP and 2MAP whereas, the root Pb concentrations at 1MAP were higher than that of 2MAP in F1 and control treatments (Table 3).

3.2. Effect of compost and inorganic fertilizer on the percentage Pb distribution into shoot and root at different plant growth stages

Table 4 on the percentage distribution in plant parts, it was observed that compost application compared to control and inorganic fertilizer reduced the movement of heavy metals from the root to the shoot as growth progressed. It was found that at 1MAP, the ratio of Pb in the maize shoot (i.e., Pb amount in the stem and leaf over that of the whole plant) was higher than that of the root in all the treatments including control and inorganic fertilizer treatments. Unlike the distribution pattern at 1MAP, a reverse was observed in the distribution at 2MAP and at harvesting. At 2MAP, the concentration in the root was more than that of the shoot except in control and inorganic fertilizer treatments. The percentage ratio of Pb in the root increased and was more than that of the shoot in all the compost treatments. At 2MAP, maize crop from contaminated soil amended with MSC had the highest percentage in the root and lowest in the shoot compared to other treatments. At harvesting, the trend in the accumulation and distribution of Pb was similar to what was observed at 2MAP and the

Table 4

Distribution ratio of Pb in the maize shoot and root in response to different treatments and sampling periods.

Treatments	1MAP		2MAP		Harvesting	
	Shoot (%)	Root	Shoot (%)	Root	Shoot (%)	Root
Control	73.5	26.5	61.0	39.0	NA	NA
MSC20	67.0	33.0	5.4	94.6	9.0	91.0
MSC40	69.0	31.0	6.0	94.0	15.0	85.0
CPC20	70.0	30.0	15.2	84.8	15.5	84.5
CPC40	59.0	41.0	24.4	75.6	33.6	66.4
F1	73.0	27.0	52.8	47.2	NA	NA

MSC20 = Mexican sunflower compost at 20 t/ha.

MSC40 = Mexican sunflower compost at 40 t/ha.

CPC20 = Cassava waste compost at 20 t/ha.

CPC40 = Cassava waste compost at 40 t/ha.

F1 = Inorganic fertilizer.

NA: Not available.

effectiveness of compost in restricting Pb mobility was similar. Higher percentage was also found in the root and lower percentage in the shoot.

3.3. Effects of compost and inorganic fertilizer on the Cd (mg/kg) concentrations in maize plant parts at different stages of development

Table 5 showed that compost addition also had significant effects on Cd accumulation by maize plant. The concentrations were reduced in compost treatments compared to those in control and F1 treatments. The highest Cd concentration was also found in the maize root from F1 treatment at 1MAP. However, likewise that of Pb, the concentrations in the leaves of maize crops in compost treatments (MSC20, MSC40 and CPC40) were significantly higher than those in the roots. Leaf Cd concentrations in the compost treated plants at 1MAP were significantly higher than those at 2MAP and harvesting except in CPC20. At 2MAP, the concentrations were reduced in all the treatments with lower concentrations in MSC20 and MSC40 compared to control and F1. The trend of distribution also changed and the concentrations were lower than those at 1MAP except in CPC20. At harvesting, there were no plants in control and F1 as mentioned above. The root Cd concentrations were more than those of the above ground parts with compost treatments at harvesting except in CPC40 which had the highest

Table 5
Effects of treatments on the Cd concentrations and distribution in maize plant parts at 1MAP, 2MAP and harvesting.

Treatments	1MAP			2MAP				Harvesting time					
	Root mg kg ⁻¹	Stem	Leaf	Root mg kg ⁻¹	Stem	Leaf	Spikelet	Root mg kg ⁻¹	Stem	Leaf	Sheath	Cob	Seed
Control	12.7 ^{aAα}	5.3 ^{aCα}	6.5 ^{aBα}	6.6 ^{aAβ}	3.2 ^{aCβ}	3.4 ^{aBβ}	NA	NA	NA	NA	NA	NA	NA
MSC20	3.9 ^{bBβ}	3.4 ^{bCα}	5.3 ^{abAα}	2.4 ^{cBγ}	3.0 ^{aAβ}	1.6 ^{bDγ}	1.8 ^{aC}	4.0 ^{aAα}	2.2 ^{bCγ}	3.7 ^{aBβ}	0.5 ^{bE}	0.8 ^{aD}	0.2 ^{aF}
MSC40	3.1 ^{bBα}	2.3 ^{bBβ}	4.1 ^{abAα}	2.2 ^{cBγ}	2.5 ^{aAα}	2.0 ^{bCβ}	1.8 ^{aD}	3.0 ^{bAβ}	0.7 ^{cDγ}	1.8 ^{bCγ}	2.8 ^{aB}	0.4 ^{aE}	0.2 ^{aF}
CPC20	3.7 ^{bAα}	3.4 ^{bBα}	3.4 ^{bBβ}	5.0 ^{abAα}	3.4 ^{aCα}	4.5 ^{aBα}	1.5 ^{aD}	3.9 ^{bAα}	3.3 ^{bBα}	0.7 ^{bCγ}	0.3 ^{bF}	0.6 ^{aD}	0.4 ^{aE}
CPC40	2.5 ^{bCβ}	2.5 ^{bBβ}	2.6 ^{bAα}	4.9 ^{bAα}	1.2 ^{bCγ}	1.2 ^{bCγ}	2.2 ^{aB}	2.5 ^{bBβ}	4.1 ^{aAα}	1.9 ^{bCβ}	0.7 ^{bE}	0.8 ^{aD}	0.5 ^{aF}
F1	11.6 ^{aAα}	4.3 ^{bAα}	3.4 ^{bCβ}	4.3 ^{bBβ}	3.4 ^{aCα}	4.4 ^{aAα}	NA	NA	NA	NA	NA	NA	NA

Means followed by the same letter in a column or row are not significantly different from each other ($P > 0.05$).

a, b, c, d, e, f were used to show the significant differences in Cd concentration among the treatments in each plant part at each sampling period.

A, B, C, D, E, F were used to show the significant differences in Cd concentration among the plant parts for each treatment and month.

α β γ were used to show the significant differences in Cd concentration for each plant part at different sampling period.

MSC20 = Mexican sunflower compost at 20 t/ha, MSC40 = Mexican sunflower compost at 40 t/ha.

CPC20 = Cassava waste compost at 20 t/ha CPC40 = Cassava waste compost at 40 t/ha, F1 = Inorganic fertilizer.

NA: Not available.

concentration in the stem. The lowest concentration of Cd was recorded in the harvested maize seeds compared to other plant parts and were not significantly different from each other in all these compost treatments.

3.4. Effects of treatments on the Cr concentrations (mg/kg) and distribution in maize plant parts at different sampling periods

Table 6 shows the concentration and distribution of Cr in maize plant parts. Like Pb and Cd, the Cr mobility to the above ground parts was restricted with compost application compared to control and F1. Concentrations were also higher in the root than above ground parts as growth progressed. In all the treatments, the concentrations in the root at 2MAP were significantly higher than those at 1MAP except in MSC40. Cr was not detected in the stem and spikelets of the maize crop in compost treatments (MSC20, MSC40 and CPC20) at 2MAP except in the stem of maize crop in CPC40. Since there were no plants from F1 and control treatments at harvesting, Cr was only considered for compost treatments and was only detected in the root of maize plant in CPC20 treatment (0.5 mg/kg).

Table 6
Effects of treatments on the Cr concentrations and distribution in maize plant parts at 1MAP, 2MAP and harvesting.

Treatments	1MAP			2MAP				Harvesting time					
	Root mg kg ⁻¹	Stem	Leaf	Root mg kg ⁻¹	Stem	Leaf	Spikelet	Root m kg ⁻¹	Stem	Leaf	Sheath	Cob	Seed
Cont	8.2 ^{bAβ}	0.7 ^{aBα}	4.2 ^{abβ}	17.0 ^{aAα}	0.7 ^{aCα}	6.7 ^{aBα}	NA	NA	NA	NA	NA	NA	NA
MSC20	3.4 ^{cAβ}	0.0 ^{cCα}	0.6 ^{bBα}	6.6 ^{cAα}	0.0 ^{cC}	0.9 ^{bBβ}	ND	ND	ND	ND	ND	ND	ND
MSC40	5.0 ^{cAα}	0.1 ^{bBα}	0.5 ^{bBα}	3.5 ^{dAβ}	0.0 ^{cCβ}	0.6 ^{bBα}	ND	ND	ND	ND	ND	ND	ND
CPC20	4.5 ^{cAβ}	0.3 ^{bBα}	1.3 ^{bbα}	6.2 ^{cAα}	0.0 ^{cC}	0.4 ^{bbβ}	ND	0.5	ND	ND	ND	ND	ND
CPC40	4.5 ^{cAβ}	0.0 ^{cCβ}	1.5 ^{bBα}	4.7 ^{dAα}	0.3 ^{bBα}	0.2 ^{cCβ}	ND	ND	ND	ND	ND	ND	ND
F1	11.5 ^{aBα}	0.7 ^{aCα}	5.5 ^{aAα}	10.8 ^{bAα}	0.8 ^{aAα}	6.1 ^{aAα}	ND	NA	NA	NA	NA	NA	NA

Means followed by the same letter in a column or row are not significantly different from each other ($P > 0.05$).

a, b, c, d, e, f were used to show the significant differences in Cr concentration among the treatments for each plant part at each sampling period.

A, B, C, D, E, F were used to show the significant differences in Cr concentration among the plant parts for each treatment and month.

α β γ were used to show the significant differences in Cr concentration in each plant part at different sampling period.

MSC20 = Mexican sunflower compost at 20 t/ha.

MSC40 = Mexican sunflower compost at 40 t/ha.

CPC20 = Cassava waste compost at 20 t/ha.

CPC40 = Cassava waste compost at 40 t/ha.

F1 = Inorganic fertilizer.

NA: Not available.

ND: Not detected.

Table 7

Transfer factors of Pb, Cd and Cr in maize plant leaves at 1MAP, 2MAP and seeds at harvesting.

TREATMENTS	1MAP			2MAP			Harvesting		
	Pb %	Cd %	Cr	Pb	Cd %	Cr	Pb	Cd %	Cr
Control	8.6	16.0	34.1	4.9	8.2	54.5	NA	NA	NA
MSC20	6.4	12.8	4.9	0.4	3.8	3.1	0.1	0.4	ND
MSC40	6.1	9.9	4.0	0.3	4.9	5.1	0.1	0.5	ND
CPC20	6.6	8.2	10.6	0.7	12.0	3.6	0.2	0.9	ND
CPC40	6.5	6.3	12.2	2.4	2.8	1.5	0.2	1.3	ND
F1	8.7	2.4	44.7	4.5	10.6	49.8	NA	NA	NA

MSC20 = Mexican sunflower compost at 20 t/ha, MSC40 = Mexican sunflower compost at 20 t/ha.

CPC20 = Cassava waste compost at 20 t/ha, CPC40 = Cassava waste compost at 20 t/ha.

F1 = Inorganic fertilizer.

NA: Not available.

ND: Not detected.

3.5. Transfer factor of Pb, Cd and Cr into leaf and seeds of maize crop in response to compost and inorganic fertilizer treatments at different growing stages

Table 7 shows the results of transfer factors and among all the three metals, Cr had the highest transfer factor in all the treatments except in those treated with MSC both at lower and higher rates at 1MAP. In these treatments, Cd was transferred more than other elements and Cr was the least. In other treatments apart from F1, Pb was the least transferred to the edible part. At 2MAP, the trend was the same in control and F1 was also similar to control at this stage with $Cr > Cd > Pb$. The least was also Pb in all the compost treatments but Cd was the highest. The transfer factors for the three metals were generally reduced at 2MAP in all the treatments but compost application reduced the transfer factors more than control and F1 where the TF for Pb from soil to the leaf was more than those in the compost treatments both at 1MAP and 2MAP. Treatment with MSC40 most effectively reduced the TF for Pb compared to other compost treatments. At harvesting, the TF was only calculated for compost treatments, and soil amendment with MSC at both rates (20 and 40 t/ha) reduced the TF for Pb compared to CPC. Soil amendment with MSC at both rates and CPC at higher rate reduced the TF for Cd at 2MAP compared to control and F1 treatments. At harvesting, the TF for Cd just like Pb was reduced in the soil treated with MSC at both rates. Compared to other heavy metals, the TF for Cr at 1MAP were the highest in all the treatments. At harvesting however, compost application reduced the TF for Cr and Cr was not detected.

On the effect of plant growing stages, Pb was transferred more at 1MAP than other periods. Cd TF varied among treatments, it was transferred at 1MAP more than other periods in all the treatments except in CPC20 and F1. Chromium TF was more at 1MAP in all the compost treatments compared to F1 and control treatments but later reduced in compost treatments at 2MAP and harvesting periods.

3.6. Bioaccumulation factors (BAF) of Pb, Cd and Cr in maize crop in response to compost and inorganic fertilizer treatments at different growing stages

Fig. 1a showed the bioaccumulation factors calculated for Pb, Cd and Cr at different growing stages. There was variations in the accumulation of these metals in the root and shoot of maize crop. Generally, the values for the Pb BAF in the root were more than those recorded for the shoot in all the treatments at every sampling period. At 1MAP and 2MAP, the Pb bioaccumulation factor (BAF) was the highest in the control and inorganic fertilizer treatments compared to others. Application of organic amendments reduced the Pb accumulation in the plant parts. The values recorded for the control and inorganic fertilizer treatments were higher than those recorded in the compost treatments. At 2MAP, the BAF for the shoot was lower than those recorded at 1MAP in all the treatments. The values recorded for the shoot in the control and inorganic treatments were however more than those grown on compost amended soil. Similarly, at harvesting, the root BAF values were higher than those of the shoot. At this stage, the data were only collected for the compost treated plants and the lowest values were recorded in the maize crop grown on soil amended with Mexican sunflower compost. Considering the different growth stages, the BAF at 1MAP was the highest in all the treatments. In the MSC20 and MSC40 treatments, the Pb BAF was conversely higher at harvesting than at 2MAP. The lowest values were recorded at harvesting in maize crop grown on soil amended with CPC40 (Fig. 1b).

Fig. 2a and b show the BAF for cadmium. As observed for Pb, the cadmium BAF in the root was more than that of the shoot at 1MAP in all the treatments except those treated with Mexican sunflower compost. The highest values were obtained in the control and inorganic fertilizer treatments for both root and shoot. At 2MAP, the Cd BAF, was still more in the root than shoot except in MSC20 and inorganic fertilizer treatments. At harvesting however, the trend was similar to that of Pb and

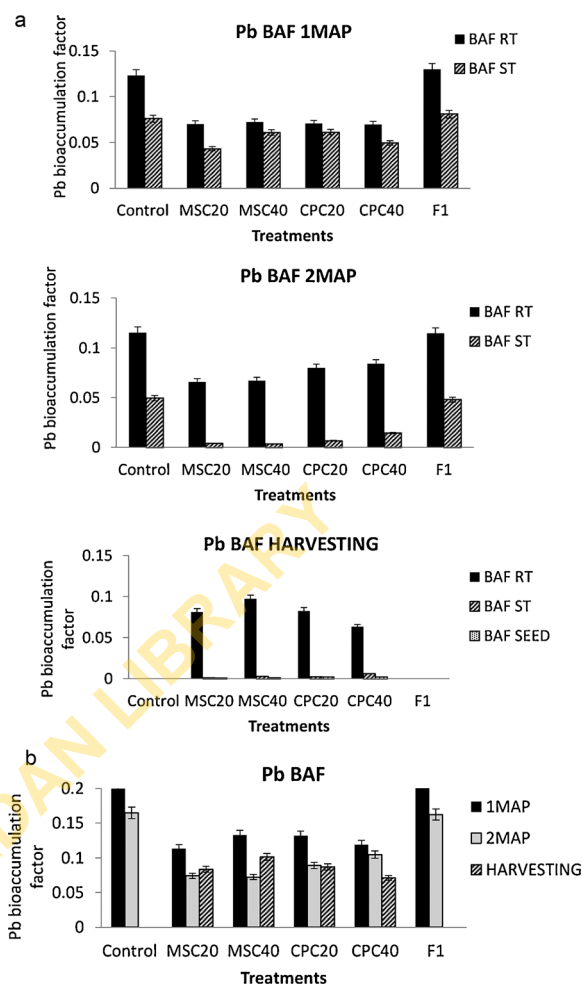


Fig. 1. (a) Pb bioaccumulation factors in the Shoot and Root at IMAP, 2MAP and Harvesting. BAF = Bioaccumulation factor; MSC20 = Mexican sunflower compost at 20 t/ha; MSC40 = Mexican sunflower compost at 40 t/ha; CPC20 = Cassava waste compost at 20 t/ha; CPC40 = Cassava waste compost at 40 t/ha; F1 = Inorganic fertilizer, BAFRT = Bioaccumulation Factor for Root; BAFST = Bioaccumulation Factor for Shoot; BAFSEED = Bioaccumulation Factor for Seed. (b) Comparative effects of sampling periods and treatments on Pb bioaccumulation factors. BAF = Bioaccumulation factor; MSC20 = Mexican sunflower compost at 20 t/ha; MSC40 = Mexican sunflower compost at 40 t/ha; CPC20 = Cassava waste compost at 20 t/ha; CPC40 = Cassava waste compost at 40 t/ha; F1 = Inorganic fertilizer.

the BAF was more in the root than that of the shoot (Fig. 2a). Comparing the BAF at different sampling periods, it was more at 1MAP than other sampling periods except in CPC 20 and CPC 40 (Fig. 2b).

Fig. 3a and b showed that among the three metals, Cr was only accumulated at 1 and 2 MAP. The BAF of Cr also varied among the treatments and between the different growing stages. At 1MAP and 2MAP, the accumulation was generally more in the control and F1 treatments compared to compost treatments. Shoot BAF values unlike what were recorded for other metals were more than those of the root in the control and F1 treatments at 1MAP. The lowest BAF values were recorded in the shoot of the maize crop grown on soil amended with Mexican sunflower compost at the two rates. The root BAF values for Cr were however greater than those of the shoot at 2MAP in all the treatments. At harvesting, its bioaccumulation factors were zero in all the compost treatments (Fig. 3a). Unlike other metals considered, the Cr BAF at 2MAP was more than that of 1MAP (Fig. 3b).

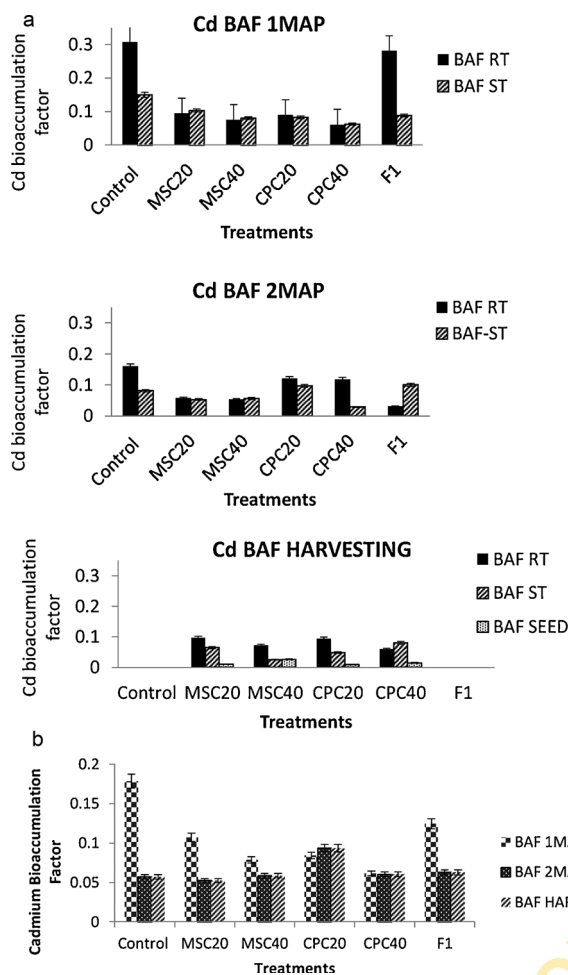


Fig. 2. (a) Cadmium bioaccumulation factors in the Shoot and Root at IMAP, 2MAP and Harvesting. BAF = Bioaccumulation factor; MSC20 = Mexican sunflower compost at 20 t/ha; MSC40 = Mexican sunflower compost at 40 t/ha; CPC20 = Cassava waste compost at 20 t/ha; CPC40 = Cassava waste compost at 40 t/ha; F1 = Inorganic fertilizer; BAFRT = Bioaccumulation Factor for Root; BAFST = Bioaccumulation Factor for Shoot. (b) Cadmium bioaccumulation factors at different sampling periods. BAF = Bioaccumulation Factor; MSC20 = Mexican sunflower compost at 20 t/ha; MSC40 = Mexican sunflower compost at 40 t/ha; CPC20 = Cassava waste compost at 20 t/ha; CPC40 = Cassava waste compost at 40 t/ha; F1 = Inorganic fertilizer.

3.7. Translocation factors (TF) of Pb, Cd and Cr in maize crop in response to compost and inorganic fertilizer treatments at different growing stages

On Fig. 4, the results of the translocation factor which is the rate of movement of metal from root to shoot showed that at 1MAP, the TIFs for Cd and Pb were more in compost than control and F1 treatments. A reverse of this was observed at 2MAP for Pb. The translocation of Cr was the least at every growing stage (Fig. 4). The translocation factor also varied at different sampling period for each metal. As observed for bioaccumulation, Pb, was translocated more at 1MAP than 2MAP and harvesting. Cd on its own had the highest translocation factors at 2MAP compared to 1MAP and harvesting except in CPC40 and MSC40 treatments where the highest were recorded at harvesting. Both elements, surprisingly were more translocated in compost treatments than control. The translocation factor was reduced in compost treatments for Cr compared to control and F1 treatments unlike Cd and Pb at all the sampling periods.

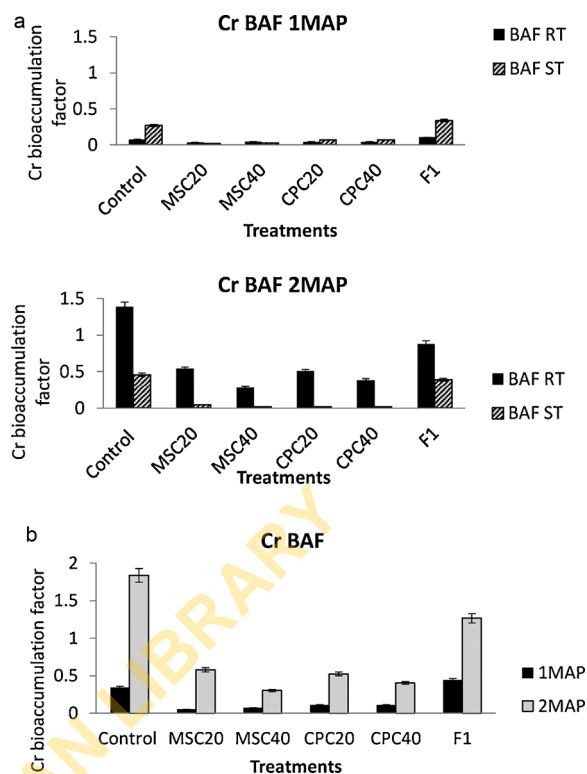


Fig. 3. (a) Chromium bioaccumulation factors in the Shoot and Root at IMAP and 2MAP. BAF = Bioaccumulation factor; MSC20 = Mexican sunflower compost at 20 t/ha; MSC40 = Mexican sunflower compost at 40 t/ha; CPC20 = Cassava waste compost at 20 t/ha; CPC40 = Cassava waste compost at 40 t/ha; F1 = Inorganic fertilizer; BAFRT = Bioaccumulation Factor for Root; BAFST = Bioaccumulation Factor for Shoot. (b) Chromium bioaccumulation factors at different sampling periods. BAF = Bioaccumulation Factor; MSC20 = Mexican sunflower compost at 20 t/ha; MSC40 = Mexican sunflower compost at 40 t/ha; CPC20 = Cassava waste compost at 20 t/ha; CPC40 = Cassava waste compost at 40 t/ha; F1 = Inorganic fertilizer.

3.8. Correlation analysis between the Pb concentration in the maize plant parts and the soil

Table 8 shows Pb concentrations in the stem and leaf is a factor of the amount in the root. The correlation between the Pb concentration in the leaf and the root was highly significant (0.80^{***}). It implies that the higher the level of Pb in the root, the higher the level that will be obtained in the leaf. Similarly, Pb concentration in the stem was also significantly related with the Pb concentration in the root (0.66^*) which simply means that as the Pb concentration is being increased in the root, the concentrations in other plant parts (stem and leaf) will also increase. Significant correlation was also found between the total Pb concentration in the leaf and in the soil (0.84^{***}). It simply means that the concentration of Pb in the leaf increases with the increase in the level of Pb in the growing medium (soil).

3.9. Heavy metal concentrations in exchangeable and organic fractions before and after application of compost

Table 9 shows that the initial concentration of Pb before application of compost in exchangeable and organically bound fractions were very high compared to what was recorded with soil amendments. The Pb concentration in the organically bound fraction was higher than that of exchangeable fraction in all the treatments including control both before and after compost application. The ratio of Pb in exchangeable fraction to organically bound fraction however decreased with compost application. The concentrations of Pb in the exchangeable and

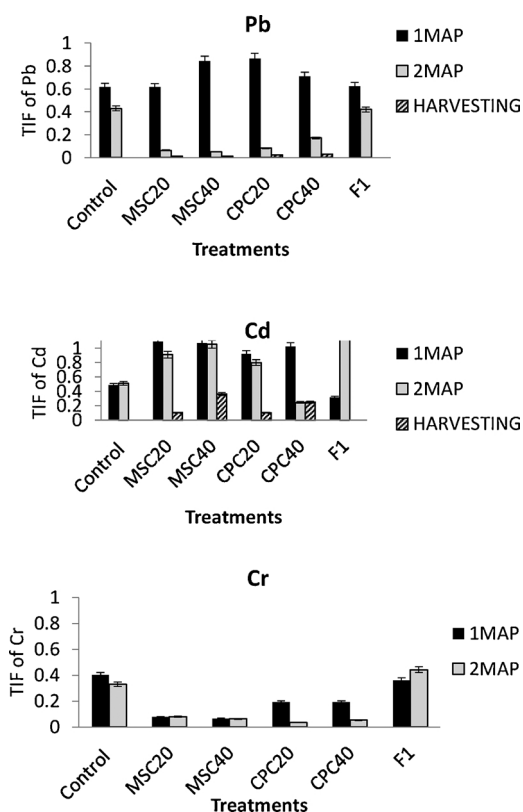


Fig. 4. Translocation factors of Pb, Cd and Cr in Maize crop in response to compost and inorganic fertilizer treatments at different growing stages. TIF = Translocation factor; MSC20 = Mexican sunflower compost at 20 t/ha; MSC40 = Mexican sunflower compost at 40 t/ha; CPC20 = Cassava waste compost at 20 t/ha; CPC40 = Cassava waste compost at 40 t/ha; F1 = Inorganic fertilizer.

Table 8

Correlation analysis between the Pb concentration in the maize plant parts and the soil.

	Cobs	Seeds	Sheath	Stem	Root	Leaf	Soil Pb
Cobs	1						
Seeds	-0.43ns	1					
Sheath	-0.19ns	-0.11ns	1				
Stem	-0.31ns	-0.40ns	0-51*	1			
Root	-0.04ns	-0.30ns	-0.22ns	-0.66*	1		
Leaf	-0.17ns	-0.47ns	-0.19ns	-0.25ns	0.80***	1	
Soil Pb	-0.13ns	-0.41ns	-0.19ns	-0.11ns	0.08ns	0.84***	1

* Significant at 0.05 level of probability.

*** Significant at 0.001 level of probability.

organically bound fractions of control and inorganic fertilizer treated soil were however, the highest. Heavy metal concentrations in the two fractions for compost treated soil were lower than what was recorded in the control and inorganic fertilizer treatments. However, application of MSC reduced the concentrations of lead and Cd in exchangeable fraction more than CPC with higher application rate of 40 t/ha performing better than lower rate (20 t/ha). This was followed by CPC at 40 t/ha. MSC at 20 t/ha gave the lowest Pb concentration in organic fraction and was lower than other compost treatments. The soil treated with CPC at 20 t/ha had the highest concentrations of Pb in both fractions compared with other compost treatments.

4. Discussion

One of the important factors contributing to the availability of any

Table 9

Effects compost rates and types and inorganic fertilizer on heavy metal concentrations in organic and exchangeable fractions.

Treatments	Organically bound fraction	Exchangeable fraction		
	Pb	Cd (mg/kg)	Pb	Cd (mg/kg)
Before compost application	6150 ^b	37.6 ^a	43.8 ^a	0.4 ^a
Control	37.6 ^g	38.0 ^a	44.0 ^a	0.4 ^a
MSC20	650.0 ^f	22.0 ^b	15.1 ^b	0.3 ^b
MSC40	881.0 ^e	22.0 ^b	3.6 ^c	0.2 ^b
CPC20	4690.0 ^c	27.3 ^b	8.0 ^d	0.4 ^a
CPC40	1010.0 ^d	18.1 ^c	11.0 ^{cd}	0.3 ^b
F1	9059.0 ^a	34.1 ^{ab}	40.0 ^a	0.4 ^a

Means followed by the same letter in a column are not significantly different from each other at $P < 0.05$ by DMRT.

MSC20 = Mexican sunflower weed compost at 20 t/ha.

MSC40 = Mexican sunflower weed compost at 40 t/ha.

CPC20 = Cassava peel waste compost at 20 t/ha.

CPC40 = Cassava peel waste compost at 40 t/ha.

F1 = Inorganic fertilizer.

element in the growing medium is the concentration of that particular element. The concentration of Pb which was higher in the maize plant tissue than other heavy metals was due to its abnormally high concentration in the studied soil thereby outcompeting other elements. Close correlation has been found between the element concentration in the growing medium and the concentration in the plant [13,35]. In this study, the Pb concentration found in the edible parts of maize (leaf and seed), though, higher than 50 mg/kg recommended by WHO/FAO [36] at every sampling period, but, it was significantly reduced in those grown on soil amended with composts.

The metal speciation carried out in this study to actually determine the effect of compost amendment on the exchangeable and organic fractions showed that these metals were highly concentrated in organic fraction more than exchangeable fraction. This probably reduced their mobility most especially Pb [37]. Some qualitative assumptions could also be made based on previous findings. For example, the dilution effect of compost on heavy metals could probably be the reason for the reduction observed in the uptake of Pb by maize crop at each sampling period in the compost treatments and this was confirmed by the previous reports which showed that addition of organic materials improves the fertility of contaminated soil by increasing the amount of nutrient ions over the heavy metal ions [16,38] and ecologically restored lead contaminated site [16]. The explanation for this was that, the higher the ratio of plant nutrients to heavy metal concentrations, the lower the uptake by plant for the latter [39,40]. This, according to Greger et al. [41] and Dalé et al. [42], was also due to either the binding of the metals to nutrient anions like phosphate ion or competition between the nutrient and toxic metal cations for the uptake sites and dilution of toxic metal ions in plant tissues. All these might be responsible for the reduction observed in the TFs and the concentrations of heavy metals in maize crop as a result of soil amendment with compost in the current study.

Amendment of substances containing high concentrations of calcium and phosphorous as were contained in the Mexican sunflower compost used for this research [16] had also been reported to reduce Pb solubility in the soil, plant uptake, and toxicity [10,11,16,43] due to formation of insoluble complexes. Phosphorous most especially has been reported to form complexes with heavy metals in the soil thereby reducing the solubility of the metals as a result of metal precipitation as pyromorphite and chloro-pyromorphite [32,44]. More importantly, the reduction in the heavy metal uptake of compost-treated maize plants compared to control plants at 1MAP and 2MAP could also be attributed to an increase in soil pH as reported by Adejumo et al. [16] for this

particular contaminated soil where pH was found to increase with compost addition from initial 5.0–7.0. This was also confirmed by the findings of David et al. [45]. This is because soil pH is said to determine the availability and leachability of heavy metals. In highly acidic condition, heavy metal ions become more soluble and the tendency for complex formation is reduced but at soil pH higher than five, the heavy metal solubility is reduced due to formation of complexes with soil matrices and hydroxyl ion while macronutrients and humic acid become more soluble [46,47]. According to Chaney et al [44], addition of compost increases soil pH and favours the solubility of plant nutrients rather than heavy metals. Fleming et al. [13] also reported that soil pH is critically important in determining the free Pb^{2+} activity in soil solution, as Pb adsorption and most precipitation reactions are favored by higher pH. For example, the surface complexation models have predicted that Pb adsorption is dominated by organic matter at soil $pH < 6$, whereas adsorption on Fe oxides is more prevalent at $pH > 6$ [48].

The general reduction in the Pb concentration of maize plants in compost treated soil could be attributed to the presence of humic and fulvic acids in the compost which have been reported to have high affinity for Pb [10,49] and the higher nutrient strength in the growing medium containing compost as in Agneta et al. [50]. Humic material has been found to have functional groups that are capable of forming insoluble complexes with heavy metals. Divalent transition metal ions such as Pb^{2+} and Cu^{2+} have also been reported to have the ability to form covalent bonding with humic acid more than alkaline earth metal ions (Ca^{2+} and Mg^{2+}) due to inability of the latter to bond covalently [10,49,51]. The findings of this research in relation to the behavior of compost on this contaminated soil could also be due to an increase in soil organic matter as confirmed by the post-cropping soil analysis result. The effectiveness of organic matter in reducing the soil Pb concentration through binding was supported by the report by Fleming et al. [13] where a decrease in extraction efficiency of Pb by Modified Morgan's universal soil extraction solution in Pb contaminated soil amended with compost was observed. According to Gary and Stephen [49], formation of strong covalent bond between humic acid and Pb^{2+} possibly occurred in contaminated soil amended with compost which might also be responsible for the lowest percentage of transfer factors recorded for Pb unlike Cd and Cr. Plant tissue Pb concentration at 1MAP was higher than the concentration at 2MAP in many cases. The higher concentration may be attributed to rapid and in-selective salt adsorption at 1MAP which was the phase of rapid vegetative growth that is usually accompanied by a marked increase in ion absorption by plant [17,52,53]. This, coupled with the slow release of nutrient ions from compost could make heavy metal concentrations to be more than those of nutrient ions at 1MAP and hence, the increase in availability and uptake of the former. At 2MAP however, the concentrations of nutrient ions compared with heavy metals must have increased, and this probably lowered the adsorption rate for the heavy metals by maize. The level of heavy metals in soil might also be reduced due to interactions between the nutrient ions and heavy metals and this interaction could either be synergistic or antagonistic [54]. This significant reduction in the plant tissue Pb concentrations at 2MAP in all the treatments most especially in the compost treated plants could be due to the binding of the heavy metals with the root cell wall and possible sequestration in the cell vacuole. It has also been reported that element initially taken up by the plants into the apparent free space (which is the space between the cell wall and the cell membrane) can be released back into the surrounding medium since they are loosely bound to the cell wall [52,55].

The eventual wilting and death of all the control plants and the plants treated with inorganic fertilizer could be attributed to high concentration of Pb which eventually led to cell death [35,51,56,57]. High salt concentration in the soil medium increases the osmotic potential of the soil thereby drawing water from the plant root. High Pb concentration has also been blamed for the inhibition of enzyme

activities and cell division at the root tips which in turn inhibits root growth [58]. However, the initial growth and survival of maize crop on the control plots despite high Pb concentration could be attributed to the adaptability nature of maize crop to toxic environment [42]. Generally, cane-type plants known as monocots are said to be tolerant due to their physiological and morphological characteristics.

The higher concentrations of heavy metals in the roots (underground biomass) which were more than those of the shoot (above ground biomass) confirmed the reports of previous experiments by Baumhardt and Welch [59], Sabey and Hart [60], Lombi et al. [61], Shridar et al. [62], Quentin and John [63] and Dalé et al. [42]. This was attributed to the inselectivity nature of the plant root as a result of mass and passive flow of nutrient in the rhizosphere across the root cell wall. Also, the binding of Pb occurs more in lignified tissues of the root epidermis than non-lignified tissue [64]. Therefore, small amount was said to be detected in the vascular tissues which probably reduces its movement to the aerial parts [65]. It has also been reported that the casparian strips of the endodermis are the major limiting factor restricting lead transport across endodermis into the central cylinder tissue [66–68]. More importantly Pb in particular is known for poor translocation from roots to shoots of a plant [69] and so high accumulation occurs in the root.

The preference given to nutrients during ion transportation in plant against the heavy metals might be responsible for the increase in the distribution ratio of Pb in the root progressively because more nutrients were released and taken up by plants in the compost treated plots. The high concentration of Pb in the leaves during the stage of active vegetative development (at 1MAP) suggested that the sink strength of the leaves was more at this stage whereas stem only serves as transporting route. The diversion of dry matter has always been reported to be in favor of leaf which served as strong sink at this growth stage followed by the stem and the root [70]. This is because the growth stage and level of plant activity are the major factors determining the amount and type of nutrients absorbed [70]. Correlation between root and leaf Pb concentrations implies that uptake by the shoot was due to accumulation in the root. This confirmed the finding that the bulk of the Pb found in above-ground parts of the plant comes from the roots [71,76]. Once the metal enters into the root, its upward movement is guaranteed owing to the attachment with other carrier molecules present within the cell that will facilitate the upward movement by breaking the endodermis and casparian strip and possibly through transpirational stream. The possibility of upward movement once in the root through transpiration pull has been confirmed by many authors [65,72,73]. In order to effectively prevent the upward movement of toxic metals in the plant, their uptake by the root must be totally prevented through precipitation and immobilization in the soil [12].

High concentration of Cd in the root also confirmed previous report on the poor mobility of Cd and only a minor portion of Cd is reportedly loaded into the xylem and transported into the above-ground part through transpiration stream [74]. The drastic reduction in Cr concentrations most especially in maize plants in compost-treated plots at harvesting shows that compost probably had high affinity for Cr more than other heavy metals. The bioaccumulation factor (BAF) which is the ratio of metal concentration in the plant tissue to the concentration in the soil and the translocation factor (TIF) which is the ratio of metal concentration in plant shoots to that of the roots are usually used to evaluate plant ability to tolerate and accumulate heavy metals. These factors were however used in this study to show the effectiveness of compost amendments and to understand the risk associated with soil contamination with heavy metals and consequent heavy metal accumulation in edible portion of maize. The treatment that reduced shoot $BAF < 1$ and $TIF < 1$ for these metals is adjudged to be effective. The BAF and TIF for all these elements were less than one in the compost treatments and Cr was found to be zero. It means that compost amendment was more effective on these metals most especially Cr. The variation in Cr translocation at different growing stages and which was

more than other metals was due to the fact that Cr was still in its Cr (vi) oxidation state which is said to be more mobile and toxic than in Cr(iii) and so easily taken up by plant at 1MAP. At 2MAP and harvesting periods, it probably must have been transformed into Cr (iii) which is less mobile with the release of more nutrients in the soil thereby reducing its uptake by maize. The amount of heavy metals found in different plant parts and at every growing stage was found to depend on the amount of assimilate partitioning and distribution to different plant parts at every growing stage.

5. Conclusions

The present study revealed that maize plant accumulated more Pb than other metals, while Cr was the lowest. Though an appreciable amount of Pb was translocated to grains of maize crops grown in heavy metal-contaminated soil and those amended with compost and that the maximum permissible level of 0.3ug/g Pb for animal and human consumption might have been exceeded several-fold, but a significant reduction in Pb accumulation was achieved by amending metal contaminated soils with compost. It reduced total heavy metal accumulation in maize crop and enhanced biomass production. Lead (Pb) uptake by maize crop (though higher than the EU permissible levels in plant tissue) at every growing stage, were significantly reduced with addition of compost compared to control. Immobilizing effects of organic amendment was seen at 2MAP and harvesting. The extent of reduction of Pb accumulation, however, depends upon the type of organic amendments applied. Crop growth stage was also found to contribute significantly to the amount of Pb found in different parts of the plant. The result also showed that compost-remediation method was more effective on Cr followed by Pb based on their Transfer, Bioaccumulation and translocation factors. Information obtained from this study will be a useful guide in using heavy-metal contaminated land for crop production and possibly prevent human contamination through food chain. This information will be valuable when develop strategies for growing crops in metal contaminated soils for animal and human consumption. Again, though the objective of this research did not intend to use maize crop for phytoremediation but from the results of translocation, transfer and bioaccumulation factors, it implies that maize crop meant for phytoremediation must be uprooted at 1MAP when the metal accumulation in the above-ground parts was at maximum. Since the concentrations in the edible parts were still above the permissible level, there will however, be need for further research to study the effect of continuous application of these composts on metal immobilization. The distribution of these metals into different soil fractions in response to compost application must also be studied.

Conflict of interest

None.

References

- [1] M.B. Ogundiran, O. Osibanjo, Heavy metal concentrations in soils and accumulation in plants growing in a deserted slag dumpsite in Nigeria, *Afr. J. Biotechnol.* 17 (2008) 3053–3060.
- [2] I.K. Kalavrouziotis, The reuse of municipal wastewater in soils, *Glob. NEST J.* 17 (2015) 474–486.
- [3] United Nations Environment Program (UNEP), *The Urban Environment: Facts and Figures. Industry and Environment. Global Environment Outlook (GEO). Latin American and the Caribbean Environment Outlook.* Mexico City, United Nations Environment Programme. Regional Office for Latin America and the Caribbean 23 (2) (2000) 61–88.
- [4] S.A. Adejumo, A.O. Togun, J.A. Adediran, M.B. Ogundiran, Effects of compost application on remediation and the growth of maize planted on lead contaminated soil, *Conference Proceedings of 19th World Congress of Soil Science, Soil Solutions for a Changing World*, (2010), pp. 99–102.
- [5] Centre for Disease Control (CDC), *Preventing Lead Poisoning in Young Children*, U.S. Department of Health and Human service Atlantic GA. Public Health service centers for disease control, 1991.
- [6] Agency for Toxic Substances and Disease Registry (ATSDR), *Toxicological Profile for Lead*, U.S. Department of Health and Human services. Public Health Services Agency for Toxic Substances and Disease Registry, Division of Toxicology and Environmental Medicine/Applied Toxicology Branch, 600 Clifton Road NE, Mailstop F 32, Atlanta Georgia 30333, 2005.
- [7] A. Singh, R.K. Sharma, M. Agrawal, F.M. Marshall, Risk assessment of heavy metal toxicity through contaminated vegetables from waste water irrigated area of Varanasi, India, *Trop. Ecol.* 51 (2S) (2010) 375–387.
- [8] R.L. Chaney, S.L. Brown, Y.M. Li, J.S. Angle, A.J.M. Baker, R.D. Reeves, S.L. Brown, F.A. Homer, M. Malik, M. Chin, Improving metal hyperaccumulators wild plants to develop commercial phytoextraction systems. Approaches and progress, in: N. Terry, G.S. Banuelos (Eds.), *Phytoremediation of Contaminated Soil and Water*, CRC Press, Boca Raton, FL, 1999.
- [9] O.'Dell Ryan, Wendy Silk, Peter Green, Victor Claassen, Compost amendment of Cu-Zn minespoil reduces toxic bioavailable heavy metal concentrations and promotes establishment and biomassproduction of *Bromus carinatus* (Hook and Arn.), *Environ. Pollut.* 148 (2007) 115–124.
- [10] H. Rennevan, R.H. Tony, A. Abir, J.M. Andy, L.J. Mike, K.O. Sabeha, Remediation of metal contaminated soil with mineral amended composts, *Environ. Pollut.* 150 (2007) 347–354.
- [11] N.S. Bolan, D.C. Adriano, R. Naidu, Role of phosphorus in (im)mobilization and bioavailability of heavy metals in the soil-plant system, *Rev. Environ. Contam. Toxicol.* 177 (2003) 144.
- [12] N. Bolan, R. Naidu, G. Choppala, J. Park, M.L. Mora, D. Budianta, P. Panneerselvam, Solute interactions in soils in relation to the bioavailability and environmental remediation of heavy metals and metalloids, *Pedologist* 53 (3) (2010) 1–18.
- [13] M. Fleming, Y. Tai, P. Zhuang, M.B. McBride, Extractability and bioavailability of Pb and As in historically contaminated orchard soil: effects of compost amendments, *Environ. Pollut.* 177 (2013) 90–97.
- [14] L.M. Shuman, Effects of organic waste amendments on cadmium and lead fractions of two soils, *Soil Sci. Plant Anal.* 29 (1998) 2939–2952.
- [15] L.P. Weng, E.J.M. Temminghoff, S. Lofts, E. Tipping, W.H. VanRiemsdijk, Complexation with dissolved organic matter and solubility control of heavy metals in a sandy soil, *Environ. Sci. Technol.* 36 (2002) 4804–4810.
- [16] S.A. Adejumo, A.O. Togun, J.A. Adediran, M.B. Ogundiran, Field assessment of progressive remediation of soil contaminated with lead-acid battery waste in response to compost application, *Pedologist* 54 (3) (2011) 182–193.
- [17] J.A. Adediran, L.B. Taiwo, R.A. Sobulo, Nutrient composition of compost and yields of two vegetable crops, *J. Sustain. Agric.* 22 (4) (2001) 95–109.
- [18] S. Salati, G. Quadri, F. Tambone, F. Adani, Fresh organic matter of municipal solid waste enhances phytoextraction of heavy metals from contaminated soil, *Environ. Pollut.* 158 (2010) 1899–1906.
- [19] X.D. Cao, L.Q. Ma, A. Shiralipour, Effect of compost and phosphate amendment on arsenic mobility in soils and arsenic uptake by the hyperaccumulator *Pierris vitata*, *L. Environ. Pollut.* 126 (2003) 157–167.
- [20] European Union, *Heavy Metals in Wastes*, European Commission on Environment, (2002) <http://ec.europa.eu/environment/waste/studies/pdf/heavymetalsreport.pdf>.
- [21] European Union, Commission regulation (EC) No. 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs, *Official Journal of European Union L364/5*, (2006).
- [22] D. Hillel, *Environmental Soil Physics*, Academic Press, San Diego CA, 1998 484 pp.
- [23] S.A. Adejumo, *Compost-Remediation of Heavy Metal Contaminated Site in Ibadan, South-Western Nigeria*. Ph.D Thesis, University of Ibadan, 2010.
- [24] S.A. Adejumo, A.O. Togun, J.A. Adediran, Comparative study of different rates of composts made from mexican sunflower (*Tithonia diversifolia*) and cassava peels on maize growth on lead contaminated soil, *J. Agric. Sci. Technol. A* (2013) 216–225 Pp 3.
- [25] J.A. Adediran, L.B. Taiwo, M.O. Akande, R.A. Sobulo, Comparative effect of organic based fertilizer and mineral fertilizer in the dry matter yield of maize, *Biosci. Res. Commun.* 11 (4) (1999) 17–24.
- [26] C.M. Amacher, D.L. Sparks, A.L. Page, P.A. Helmke, M.A. Tabatabai, C.T. Johnson, M.E. Sumner, J.M. Bartels, J.M. Bigham (Eds.), *Selective Extraction of Nickel Cadmium and Lead from Soil. SSA Methods of Soil Analysis Part-3 Chemical Methods*, Soil Science Society of America Inc. American Society of Agronomy, Inc., Madison, Wisconsin USA, 1996, pp. 739–767 No 5. pp.28.
- [27] M. Smejkalova, O. Milkanova, L. Boruvka, Effects of heavy metal concentrations on biological activity of soil micro-organisms, *Plant Environ.* 7 (2003) 321–326.
- [28] J.U. Anderson, Improved pretreatment for mineralogical analyses of samples containing organic matter, *Clays Clay Miner.* 10 (1963) 380–388.
- [29] L.M. Lavkulch, J.H. Wiens, Comparison of organic matter destruction by hydrogen peroxide and sodium hypochlorite and its effects on selected mineral constituents, *Soil Sci. Soc. Am. Proc.* 34 (1970) 755–758.
- [30] J.U. Anderson, G.A. O'Connor, Production of permanganate ion by sodium hypochlorite treatment to remove soil organic matter, *Soil Sci. Soc. Am. Proc.* 36 (1972) 973–975.
- [31] L.M. Shuman, Sodium hypochlorite methods of extracting micronutrients associated with soil organic matter, *Soil Sci. Soc. Am. J.* 46 (1983) 656–660.
- [32] M.B. Ogundiran, *Assessment and Chemical Remediation of Soil Contaminated by Lead Acid Battery Wastes in Lalupon Village Oyo State. Nigeria*. Ph.D Thesis, University of Ibadan, 2007.
- [33] M. Ghosh, S.P. Singh, A comparative study of cadmium phytoextraction by accumulator and weed species, *Environ. Pollut.* 133 (2005) 365–371.
- [34] Jaswant Singh, Suraj K. Upadhyay, Rajaneesh K. Pathak, Vidhu Gupta, Accumulation of heavy metals in soil and paddy crop (*Oryza sativa*), irrigatedwith

- water of Ramgarh Lake, Gorakhpur, UP, India, *Toxicol. Environ. Chem.* 93 (2011) 462–473.
- [35] I.V. Seregin, V.B. Ivaniov, Physiological aspects of cadmium and lead toxic effects on higher plants, *Russ. J. Plant Physiol.* 48 (2001) 606–630.
- [36] WHO/FAO, Houston, United States of America, Joint FAO/WHO Food Standard Programme Codex Alimentarius Commission 13th Session. Report of the Thirty Eight Session of the Codex Committee on Food Hygiene (2007) ALINORM 07/30/13.
- [37] D.J. Ashworth, B.J. Alloway, Influence of dissolved organic matter on the solubility of heavy metals in sewage-sludge-amended soils, *Commun. Soil Sci. Plant Anal.* 39 (2008) 538–550.
- [38] J.B. Timothy, P. John, J.B. Hugh, S. Misty, Phytoextraction of Pb and Cd from a superfund soil: effects of amendements and croppings to mineral provisions, *J. Exp. Bot.* 42 (2001) 729–737.
- [39] S. Trivedi, L. Erdei, Effects of cadmium and lead on the accumulation of K and Ca and on the influx and translocation of K in wheat of low and high K status, *Physiol. Plant* 84 (1992) 94–100.
- [40] L. Ekvall, M. Greger, Effects of environmental biomass-producing factors on Cd uptake in two Swedish ecotypes of *Pinus sylvestris*, *Environ. Pollut.* 121 (2002) 401–411.
- [41] M. Greger, E. Brammer, S. Lindberg, G. Larsson, J. Idestam-Almquist, Uptake and physiological effects of cadmium in sugarbeet related to mineral provisions, *J. Exp. Bot.* 42 (1991) 729–737.
- [42] P. Dalé, R. Jüraté, L. Loreta, L. Albinas, Growth and metal accumulation ability of plants in soil polluted with Cu, Zn, and Pb, *Ekologija* 1 (2006) 48–52.
- [43] N. Roongtanakiat, Y. Osotsapar, C. Yindiram, Effects of soil amendment on growth and heavy metals content in vetiver grown on iron ore tailings, *Kasetsart J. (Nat. Sci.)* 42 (2008) 397–406.
- [44] R.L. Chaney, S.L. Brown, Y.M. Li, J.S. Angle, T.I. Stuczynski, W.L. Daniels, C.L. Henry, G. Siebec, M. Malik, J.A. Ryan, H. Compton, Boston, MA, Progress in Risk Assessment for Soil Metals, and in-Situ Remediation and Phytoextraction of Metals from Hazardous Contaminated Soils. USEPA. “Phytoremediation; State of Science” (2000) May 1–2, 2000.
- [45] J.W. David, C. Rafael, M.P. Bernal, Contrasting effects of manure and compost on soil pH, heavy metal availability and growth of *Chenopodium album* L. in a soil contaminated by pyritic mine waste, *Chemosphere* 57 (2004) 215–224.
- [46] Q.B. He, B.R. Singh, Cadmium availability to plants as affected by repeated applications of phosphorus fertilizers, *Acta Agric. Sci. B* 45 (1995) 22–31.
- [47] S. Sauve, M. McBride, W. Hendershot, Soil solution speciation of lead II: effects of organic matter and pH, *Soil Sci. Soc. Am. J.* 62 (1998) 618–621.
- [48] J.P. Gustafsson, C. Tiberg, A. Edkymish, K.D. Berggren, Modelling lead (II) sorption to ferri hydrite and soil organic matter, *Environ. Chem.* 8 (2011) 485–492.
- [49] W.V. Gary, J.D. Stephen, *Environmental Chemistry (A Global Perspective)* 12 Oxford University Press, 2000, pp. 239–258.
- [50] G. Agneta, G. Greger, K. Holm, B. Bengt-Erik, Influence of nutrient levels on uptake and effects of mercury, cadmium and lead in water spinach, *J. Environ. Qual.* 33 (2004) 1247–1255.
- [51] G.L. Wayne, Y. Ming-Ho, *Introduction to Environmental Toxicology: Impacts of Chemicals upon Ecological Systems*, 3rd edition, Lewis Publishers, United States of America, 2004, pp. 219–233 Pp 9.
- [52] J.F. Sutcliffe, Mineral salt absorption in plants, in: P.F. Wareing, A.W. Galston (Eds.), *International Series of Monograph on Pure and Applied Biology. Division of Plant Physiology*, 4 The Villafield Press, Bishopbriggs, Glasgow, Great Britain, 1962, pp. 47–71.
- [53] W.B. Akanbi, Growth, Nutrient Uptake and Yield of Maize and Okro as influenced by Compost and Nitrogen Fertilizer Under Different Cropping Systems. Ph.D Thesis, University of Ibadan, 2002 pp X+ 222.
- [54] I.K. Kalavrouziotis, P.H. Koukoulakis, F. Papadopoulos, Heavy metal inter-relationships in soil in the presence of treated waste water, *Glob. NEST J.* 11 (4) (2009) 497–509.
- [55] H. Marschner, *Mineral Nutrition of Higher Plants*, Academic press, London, United Kingdom, 1995, pp. 256–287 23.
- [56] B. Pourrut, M. Shahid, C. Dumat, P. Winterton, E. Pinelli, Lead-induced phyto-toxicity mechanism, lead uptake, toxicity and detoxification in plants, *Acta Biol. Hung.* 42 (4) (1991) 331–344.
- [57] I.V. Seregin, L.K. Shpigur, V.B. Ivaniov, Distribution and toxic effects of Cd and Pb on maize roots, *Russ. J. Plant Physiol.* 51 (2004) 525–533.
- [58] S.O. Eun, H.S. Youn, Y. Lee, Lead disturbs microtubules organization in the root meristem of Zea mays, *Physiol. Plant* 110 (2000) 357–365.
- [59] G.R. Baumhardt, L.F. Welch, Lead uptake and corn growth with soil applied lead, *J. Environ. Qual.* 1 (1972) 92–94.
- [60] B.R. Sabey, W.E. Hart, Land application of sewage sludge. Effect on growth and chemical composition of plants, *J. Environ. Qual.* 4 (1975) 252–256.
- [61] E. Lombi, F.J. Zhao, S.J. Dunham, S.P. McGrath, Cadmium accumulation in populations of *Thlaspi caerulescens* and *Thlaspi goesingense*, *New Phytol.* 145 (2000) 11–20.
- [62] M.K.C. Shridar, J.O. Etaghene, G.O. Adeoye, Remediation of lead contaminated soil using physicochemical and phytoremediation technique: experience from South West Nigeria, *Plant Foods Hum. Nutr.* 56 (4) (2003) 313–324.
- [63] M.F. Quentin, P. John, Plant Response and Accumulation of Lead, Cadmium and Barium from a Superfund Site Soil, (2003).
- [64] A. Kosobrukhev, I. Knyazeva, V. Mudrik, Plantago major plants responses to increase content of lead in soil: growth and photosynthesis, *Plant Growth Regul.* 42 (2004) 145–151.
- [65] P. Sharma, S.D. Rama, Lead toxicity in plants, *Braz. J. Plant Physiol.* 17 (2005) 1677–2420.
- [66] I.V. Seregin, V.B. Ivaniov, Histochemical investigation of cadmium and lead distribution in plants, *Fiziol. Rast.* 44 (1997) 915–921.
- [67] R.M. Abdul, A.K. Digidem, O. Aylin, V. Anastasia, Heavy metal accumulation and detoxification mechanism in plants, *Turk. J. Bot.* 25 (2001) 111–121.
- [68] S. Verma, R.S. Dubey, Lead toxicity induces lipid peroxidation and alters the activities of antioxidant enzymes in growing rice plants, *Plant Sci.* 164 (2003) 645–655.
- [69] K. Cezary, B.R. Singh, Fractionation and mobility of copper, lead and zinc in soil profiles in the vicinity of a copper smelter, *J. Environ. Qual.* 30 (2001) 485–492.
- [70] M. Ashraf, F. Hussain, Dry matter and nitrogen distribution at maturity of three rice (*Oryza sativa* L.) cultivars exposed to ammonia at two growth stages, *J. Agron. Crop Sci.* 191 (2005) 125–129 (2005). Blackwell Verlag, Berlin ISSN 0931-2250.
- [71] I.K. Kalavrouziotis, P.H. Koukoulakis, F. Papadopoulos, P. Psoma, Interrelationships of metal transfer factor under wastewater reuse and soil pollution, *J. Environ. Manage.* 216 (2018) 328–336.
- [72] M.J. Blaylock, D.E. Salt, S. Dushenkov, O. Zakarova, C. Gussman, Y. Kapulnik, B.D. Ensley, I. Raskin, Enhanced accumulation of Pb in Indian mustard by soil applied chelating agents, *Environ. Sci. Technol.* 31 (1997) 860–865.
- [73] M.J. Blaylock, J.W. Huang, Phytoremediation of toxic metals, in: I. Raskin, B.D. Ensley (Eds.), *Using Plants to Clean up the Environment*, John Wiley & Sons Inc., New York, NY, 1999, pp. 53–70.
- [74] A. Polle, A. Schu'tzendu'bel, Heavy metal signalling in plants: linking cellular and organismic responses, in: H. Hirt, K. Shinozaki (Eds.), *Plant Stress Responses. Topics in Current Genetics* 4, Springer-Verlag, Berlin, Heidelberg, 2003, pp. 1–29.
- [75] G. Brümmer, J. Gerth, U. Herms, Heavy Metal Species, Mobility and Availability in Soils, *Z. Pflanzenernaehr. Bodenk.* 149 (1986) 382–389.
- [76] P.B.A.N. Kumar, V. Dushenkov, H. Motto, I. Raskin, Phytoextraction: the use of plants to remove heavy metals from soils, *Environ. Sci. Technol.* 29 (5) (1995) 1232–1238.
- [77] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, *Anal. Chem.* 51 (1979) 844–851, <https://doi.org/10.1021/ac50043a017>.