

Heavy Metal Concentrations in Some Vegetables Grown in a Farm Treated With Urban Solid Waste in KuruJantar, Nigeria.

Abstract

The use of dumpsite soils as organic manure is wide spread in developing countries like Nigeria. This study investigates the concentration of some heavy metals in vegetables grown in a farm treated with dumpsite soils in KuruJantar, Jos-South. Soil samples and vegetables from the farm were collected and prepared using standard analytical procedures. The concentrations of metals in both soil and vegetables were determined using atomic absorption spectrophotometer (AAS). The results showed that the farm was polluted with the metals (Cd, Cr, Cu, Mn, Fe, Pb, Zn, Ni) determined. The Enrichment Factor (EF) showed that some metals had minimal enrichment while Cd(13.93) had significant enrichment at the farm. The Pollution index (PI) calculations showed that at the farm, the contamination pollution ranged from very slight to very severe. The overall order of the metals at the dumpsite was Fe>Mn> Zn> Cu> Cr> Ni>Pb> Cd while the order of the metal concentrations at the farm was Fe>Mn> Zn> Ni> Cd>Pb. The data obtained in the study were analyzed using Pearson correlation analysis. The results showed perfect positive correlation values above 0.9 between the farm and the dumpsite, which indicated that there was a strong association or similarity between them. In spinach plant species, metal concentrations decreased in the order Fe>Zn>Mn>Cd>Pb; in Cabbage, Mn> Fe> Zn>Cu>Cd; in Radish, Fe>Mn>Cu>Cr>Zn; in pepper, Fe>Cu>Mn>Ni. In general, the metal concentrations were below the recommended limit of USEPA and FEPA standards for agricultural soils and vegetables except for Cd in vegetables. The concentrations were however higher in the farm than in the control. Thus, the farm was polluted with heavy metals from the dumpsite soils.

Keywords: Heavy metals, dumpsite, vegetables, pollution, organic manure, Enrichment Factor

Introduction

The use of dumpsite soils as organic manure is widespread in Plateau state, Nigeria. This practice has been shown to improve soil properties such as organic matter, nutrients, porosity, aggregate stability, bulk density and water retention, and as a result, increase plant productivity [1, 2]. It is however a known fact that some of the waste products contain hazardous metals such as Ni, Pb, Cd, Zn, and Hg [3], which perturb the distribution and concentration of these metals in the environment. Recent studies have also revealed that the waste dumpsite can transfer significant levels of these toxic and persistent metals into the soil environment [4,5].

Heavy metals are toxic pollutants that therefore, severely limit the beneficial use of dumpsite soil as organic manure. Heavy metals are very harmful because of their non-

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biodegradable nature, long biological half-life and their potential to accumulate in different body parts [6]; even low concentrations of heavy metals can also be toxic because there is no good mechanism for their elimination from the body. The bioaccumulation of metals as a major route through which increased levels of the pollutants are transferred across food chain web has been reported [7]. The presence of heavy metals in the ecosystem therefore, has far reaching implication directly to the soil and indirectly to man. Metal uptake by plants can be affected by several factors including metal concentrations in soils, soil pH, cation exchange capacity, organic matter, types and varieties of plants, and plant age [8]. It is generally accepted that the metal concentration in soil is the dominant factor and the concentrations of heavy metals are higher in soils than vegetables grown on the same soils [9]. It has also been reported that vegetable crop plants have high ability to accumulate metals from the environment, which may pose risks to human health when they are grown on or near contaminated lands and consumed. Thus, accumulation of heavy metals in the edible parts of vegetables represents a direct pathway for their incorporation into the human food chain [10, 11]. The health risk will depend upon the chemical composition of the waste material, its physical characteristic, types of vegetables cultivated and the consumption rate [12, 13].

This study ~~therefore~~ assessed the uptake of metals by plant vegetables grown on a farm treated with urban solid waste in KuruJantar, Jos-South.

Materials and Methods

Soil and Plant Sampling

The soil and vegetable samples for this analysis were collected randomly from a farm located about 200m from KuruJantar dumpsite on longitude 08° 53'E and latitude 09° 42' N. The vegetables, including spinach, cabbage, radish, tomato, and pepper, were harvested at the same spots where the soil samples were collected. The vegetables harvested were spinach, cabbage, radish, and tomatoes.

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and pepper, and were washed with distilled water to remove soil particles. The soil samples were air-dried, crushed and sieved to pass through a 2mm sieve. Similarly, the vegetables were cut with plastic knives before drying in oven at 70⁰C until stable weights were obtained. The dried samples were ground in mortar and sieved. .

Analysis of the Heavy Metal Content in Soil and Vegetable Samples

———— Triplicate samples of 1.0g of the sieved soil samples were digested with 25mL of a mixture of hydrochloric acid (HCl) and trioxonitrate (v) acid (HNO₃) in the ratio of three to one parts by volume respectively at 120⁰C on a water bath in a fume cupboard. The solution was heated to dryness and the residue was re-dissolved in 5mL of 2.0M HCl [14 – 16]. Digested samples were filtered into a 100ml volumetric flask and made up to the mark with distilled water.

Triplicate (1g) of the sieved vegetable samples were weighed into different conical flasks and digested with conc. HNO₃ to a clear solution. Digested samples were filtered into a 100mL volumetric flask and made up to the mark with distilled water [17]. The concentrations of the metals in the digested soil and vegetable samples were determined using Buck scientific VGP 210 Atomic Absorption Spectrophotometer at wavelengths specific to each metal. The metals analyzed in both samples were: Pb, Cu Cr, Ni, Zn, Fe, Cd, Mn.

Calculation of Enrichment Factor (EF) and Pollution Index (PI)

The enrichment factors of the heavy metals in soil were calculated with the formula as reported by other researchers [19]

$$EF = \frac{C(M-S)/C(Fe-S)}{C(M-C)/C(Fe-C)}$$

Where $C(M-S)$ concentration of metal in the sample, $C(Fe-S)$ concentration of reference metal in the sample, $C(M-C)$ concentration of metal in the control $C(Fe-C)$ concentration of reference metal in the control. The control was a farm not treated with the solid waste.

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The contamination/pollution index(*PI*) was calculated as the ratio between metals effectively measured by chemical analysis to the reference value [20].The conversion formula [19] for the pollution index was also used and the reference standard used in the calculation was the Federal Environmental Protection Agency [22] target value.

$$\text{Pollution index (PI)} = \frac{\text{Concentration of metal in soil}}{\text{Standard recommended maximum value in soil}}$$

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pH Determination

Triplicate quantities (20g) of air-dried of the soil samples were weighed into a 50mL beaker and 20mL of distilled water was added. The mixture was allowed to stand for 30 minutes with occasional stirring using a glass rod. The electrode of the calibrated pH meter, MI 806 pH/EC/Temperature Portable Meter inserted into the partly settled suspension and the pH value read [14].

Organic Matter Determination

The soil samples were ground to pass through 0.5mm sieve after which they were weighed in duplicate and transferred to 250mL Erlenmeyer flasks. Exactly 10mL of 1M potassium dichromate was pipette into each flask and swirled gently to disperse the soil followed by addition of 20mL of concentrated, tetraoxosulphate (IV) acid. The flask was swirled gently until soil and reagents were thoroughly mixed. The mixture was then allowed to stand for 30 minutes on a glass plate to allow for the oxidation of potassium dichromate to chromic acid. Distilled water (100mL) was added then 3-4 drops of ferroin indicator, after which the mixture was titrated with 0.5M ferrous sulphatesolution. A blank titration was similarly carried out [14]. The percentage organic carbon is given by the following equation:

$$\text{Percentage organic carbon} = \frac{M1e1K2Cr2O7 - M2e2FeSO4 \times 0.0031 \times 100 \times F}{\text{Mass(g) of air dried soil}}$$

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F= correction factor (1.33), $M_1 = \text{mole of } K_2 Cr_2 O_7$, $e_1 = \text{volume of } K_2 Cr_2 O_7$, $M_2 = \text{mole of } FeSO_4$, $e_2 = \text{volume of } FeSO_4$, % = organic matter in soil = organic carbon $\times$ 1.729.

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Total Nitrogen: The total Nitrogen was determined using the kjeldahl digestion method. The ammonia in the digest was absorbed into boric acid mixed indicator solution and then titrated with standard 0.01M H_2SO_4 . The soil samples (2g) were digested into 50ml solution, and then 20mL of the digest were used for the determination of total nitrogen.

Available Phosphorous: This was extracted using bray P1 and P2 extractant and P in the extract was measured with spectrometer (model spectronic 20D) using the molybdenum blue colour method.

Exchangeable Bases: These were extracted with 1M NH_4OAC (pH 7) solution. The concentrations of K and Na in the extract were determined using Flame analyser (Model FP640) while Mg was obtained by versenate titration.

Cation Exchange Capacity (CEC): cation exchange capacity by the 0.01M silver-thiourea method [23].

Statistical Analysis

The data obtained in the study were analyzed using Pearson correlation analysis. Correlations were calculated to measure the degree of linear relationship between plant metal concentrations and soil properties/soil metal concentrations.

RESULTS AND DISCUSSION

The physicochemical properties have been reported to have profound influence on the mobility and bioavailability of heavy metals and uptake by plants [18, 19]. Therefore, the properties of the

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soils collected from the dumpsite and farm such as pH, cation exchange capacity (CEC), electrical conductivity (EC) and organic matter (OM) were determined. The results of the physicochemical properties are presented in Table 1. The results showed that the pH at the dumpsite was slightly alkaline with a pH of 8.30. This may be attributed to the buffering effect of soil organic matter against pH changes in addition to the release of basic cations during the organic matter decomposition [5].

The pH of the soil collected from the farm was 6.71 which indicated that the soil was slightly acidic. This could be attributed to the inorganic fertilizer and other chemicals used on the farms. This was also expected as most soils in the tropics have their range from acidic to slightly neutral pH [5]. The pH levels that are acidic tend to have an increased micronutrient solubility and mobility as well as increased heavy metal concentration in the soil [20]. The results of the available phosphorus in the dumpsite soil were very similar to that in the farm ranging from 0.03 – 0.12 mg/kg. The concentration of phosphorus contributes to the growth of plants [22].

The cation exchange capacity is the amount of exchangeable cation per unit weight of dry soil that plays a very important role in soil fertility. The concentrations of the exchangeable cations (CEC) in cmol/Kg at the dumpsite were 1.86 (Na), 21.60 (K), 5.20 (Mg) and 11.12 (Ca) while at the farm the values were 0.30, 0.76, 0.50 and 4.65 respectively. However, the concentration at the farm was higher than the control, which indicated that the dumpsite could be implicated with the amendment of soil properties of the farm. The CEC is directly related to the capacity of adsorbing heavy metals since the adsorption behaviour depends on combination of the soil properties and the specific characteristics of the element [24].

The organic matter (OM) content of the dumpsite soil was 5.8% while the farm had 2.40% and the control had 1.12%. The OM content of the control site was significantly lower compared to the farm and dumpsite soils (see Table 1). This might be attributed to the activities of the microorganisms involved in the organic matter decomposition from the dumpsite

158 thereby,accumulating more organic matter in the soils [18]. Thus, the results showed that the use
159 of the urban solid waste as manure influenced the organic matter in the farm. The organic matter is
160 one of the factors that may reduce the ability of metals to be phytotoxic in the soil due to metal-
161 organic complexation [18]. The organic matter content of the soil plays an important role in
162 absorption reaction in the soil and total cation exchange site [21]. The organic matter is also an
163 important indicator of the soil as a rooting environment [20].

164 **Table 1: Physicochemical Properties of the Dumpsite andFarm Treated with the Dumpsite**
165 **Waste.**

167		Dumpsite	Farm	Control
168	pH	8.30	6.71	6.15
169	Organic Matter(%)	5.80	2.40	1.12
170	Total Nitrogen (%)	0.63	0.35	0.35
171	Exchangeable Na (cmol Kg ⁻¹)	1.86	0.30	0.24
172	Exchangeable K (cmolKg ⁻¹)	21.60	0.76	0.87
173	Exchangeable Mg (cmol Kg ⁻¹)	5.20	0.50	0.45
174	Exchangeable Ca (cmol Kg ⁻¹)	11.12	4.65	1.80
175	Available P (mg/Kg)	0.11	0.11	0.03
176	CEC (cmol Kg ⁻¹)	40.50	6.53	3.68
177	Texture	Sand	Sand	Sand

178 Control = a farm not treated with the solid waste.

179 The concentration of the exchangeable cations (CEC) in the dumpsite soil was 40.50
180 ~~emolkg⁻¹cmol Kg⁻¹~~ which was much higher than 6.53~~cmol Kg⁻¹emolkg⁻¹~~ from the farm.The
181 concentrations of the exchangeable cations were however, higher than the control which
182 implicated the use of the dumpsite soil to have affected the farm positively. This could be due to
183 difference in the heterogeneous nature of waste[5], which is expected to impact differently on soil

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properties. The available phosphorous in the farm and dumpsite were the same 0.11mg/kg which was higher than the value for the control farm (0.03mg/kg). The percentage of nitrogen was 0.35%.

The physicochemical parameters indicated that the organic matter, cation exchange capacity, nitrogen and phosphorus content of the farm were moderate with moderate values of C:N ratio implicating the urban solid waste to be fertile. Thus, the results of the physicochemical parameters revealed that the soils were fertile to support plant growth but this cannot be compared to the adverse effect of using this solid waste as manure. This may serve as a source of metals into the food chain.

The heavy metal concentrations in soil samples from the dumpsite, farm and controls were determined and the results are presented in Mean $\pm$ Standard Deviation (Table 2). The results showed that the mean concentrations of copper (Cu) in the dumpsite and farm soil samples were 130.19 and 63.23mg/kg respectively. Therefore, the value at the dumpsite was above the normal range 2-100 mg/kg [9] in the mineral soil environment and is significantly above the data obtained for the control samples. Copper is very toxic to most plants, and highly toxic to mammals [13]. Copper concentration levels above normal range are highly dangerous and pose health risks to the environment. The concentration of Cu in this study was lower than the values reported at Lagos metropolis, Nigeria [13].

The concentration of manganese (Mn) at the dumpsite (422.72mg/Kg) was much higher than the farm treated with the waste from the dumpsite which had a value of 219.60mg/kg. However, the concentration of Mn at the farm was much higher than the control. The higher levels of Mn found in the farm could be closely related to the pollutants from the dumpsite. The values of Mn in this study were much higher than the values reported by other researchers [25]. However, the values were within WHO/FAO recommended maximum value (2000mg/kg) for agricultural soil as

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reported by [17, 24]. The results obtained for the different soil samples from the dumpsite and the farm show that they are highly contaminated with iron when compared with the control values. The mean concentration value of 2436 mg/kg at the dumpsite and 408 mg/kg were within the normal range of mineral soil environment of 300-500,000 mg/kg reported for naturally occurring heavy metal concentrations for soil [22, 23]

The concentration of zinc found in the soil samples at the dumpsite (246.39mg/Kg) and farm (66.23mg/Kg) were within the normal range 10-300 mg/kg for agricultural soil. The results of the dumpsite and the farm showed that they were contaminated with Zn when compared with the control values. Zinc constitutes an essential element (micronutrient), but it is toxic to crop plants especially vegetables at the level of 400 mg/kg in the soil [14].

The concentrations of Cd in the dumpsite soil sample (28.06mg/Kg) was higher than the WHO/FAO maximum permissive limits while the concentration in the farm soil sample (2.30mg/Kg) was lower than the maximum permissive limit. Similarly, the concentrations of Ni in the dumpsite and farm soil samples were lower than the maximum permissive limit (Cd 3; Ni 75 [14]). However, the concentrations of these metals at the dumpsite and farm were higher than the control values. Therefore, there are apparent indications of the adverse effects of the dumpsite on the values of metals as compared to their values in the control. Similar observations have been reported [20 and 21]. This result is also consistent with previously published data [14].

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Table 2. Concentration of Metals in Soil Samples Collected from the Dumpsite

andFarm.

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Element	Farm			
Dumpsite	Control	F	Control	
Cu	130.19±2.30	2.45±0.05	63.23±25.36	6.07±0.04
Mn	422.72±28.67	28.99±9.11	219.60±57.88	45.20± 9.55
Fe	2436±105.95	249.00±7.43	408.20±78.38	74.18±42.22
Cd	28.06±2.03	ND	2.30±0.14	0.03±0.01
Ni	26.32±2.85	ND	15.60±0.12	3.03±0.62
Zn	246.39±10.75	8.92±3.12	66.23±8.96	23.08± 5.02
Pb	23.30±5.70	9.13±3.25	25.33±0.38	4.58±1.01

Comment [MM10]: Farm?

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The metal concentration correlation analysis between the farm and the dumpsite was conducted using Pearson correlation coefficient (r) values to determine the level of association. The results showed perfect positive correlation values above 0.9 between the farms and the dumpsites, which indicated that there was a ~~strong-significant~~ association or similarity between them. At both p<0.05 and p<0.01 level ~~of significant, all the correlations were significant~~. This implies that the similarity in the concentrations between the farm and dumpsite was quite high. The concentrations of the metals in the farm (F) decreased in the order Fe > Mn > Zn > Pb > Cu > Ni > Cd.

Enrichment Factor (EF) of the heavy metals in soil from farm showed that Cu (0.49), Mn (0.88), Fe (1), Ni (0.94), Zn (0.52) and Pb (0.88) had minimal enrichment while Cd (13.93) had significant enrichment (see Table 3).

Table 3: Enrichment Factor (EF) and Contamination /Pollution (C/P) Index of Heavy Metals in Soil samples from the Farm (F)

	Cu	Mn	Fe	Cd	Ni	Zn	Pb
C (M –S)	16.32	219.6	408.20	2.30	15.60	66.33	22.27
C (Fe- S)	408.20	408.20	408.20	408.20	408.20	408.20	408.20
C (M-C)	6.07	45.20	74.18	0.03	3.03	23.08	4.58
C (Fe-C)	74.18	74.18	74.18	74.18	74.18	74.18	74.18
EF	0.49	0.88	1.00	13.93	0.94	0.52	0.88
P/ I	0.90	0.50	0.08	0.77	0.45	0.22	0.09

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C (M –S) concentration of metal in the sample; C (Fe- S) concentration of reference metal in the sample; C (M-C) concentration of metal in the control; C (Fe-C) concentration of reference metal in the control.

The results of the calculated enrichment (EF) in this research showed that Mn, Ni, and Pb had enrichment factors close to unity, Cd was greater than 10, while Cu and Zn are lacking (Table 3). The use of urban solid waste as manure could be implicated with the high enrichment of Cd at the farms. The soil Cd could also be due to the application of phosphate fertilizers [26]. This therefore poses serious concern as crops grown on these farms could bioaccumulate the metal. The Pollution Index (P/I) of the metals at the farm ranged from 0.08 to 0.90 which showed that the farm had very slight contamination to very severe contamination with the metals.

Metal Content in Vegetables grown on the Farm

The concentration of the metals obtained in the leafy vegetables (spinach and cabbage), root vegetable (radish) and fruit vegetables, (tomato and pepper) are presented in Table 5. The main

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283 sources of heavy metals to vegetable crops are their growth media from which these are taken up
284 by the roots. A better understanding of heavy metals sources, their accumulation in the soil and
285 subsequent uptake by plant species seem to be particularly important in present day research on
286 risk assessment [27]. The uptake of metal ions has been shown to be influenced by the metal
287 species and plant parts-[26].The results of the metal content in vegetables grown on the farm in
288 this study showed that spinach, bio-accumulated the metals Fe, Mn, Zn, Cd, Ni and Pb in the order
289 Fe > Mn > Zn > Cd > Ni > Pb (Table 5). This could be a reflection of the concentrations of the metals
290 in the soil. Leafy vegetables have been shown to accumulate relatively higher concentrations of
291 heavy metals than fruit vegetables [24]. The observed concentrations of the metals in the vegetables
292 were compared with the recommended limit as established by the FAO/WHO in 1999 to assess the
293 levels of food contamination. The concentration of Cd (3.21 mg/kg) was much higher than the
294 recommended maximum levels in vegetables (0.20 mg/kg) [28]. Cadmium is relatively easily taken
295 up by the food crops especially by vegetables in the addition to foliar absorption of Cd from
296 atmospheric deposition on plant leaves [29]. Several studies have indicated that vegetables grown
297 in heavy metals contaminated soils have higher concentrations of heavy metals than those grown
298 in uncontaminated soils [29]. Cd is relatively mobile in soil under range of pH, O.C and CEC
299 conditions. This shows that some other soil factors in addition to the total soil contents of the
300 metals also influenced metal uptake. The other metals were within the recommended maximum
301 limits in vegetables with Mn and Fe (500.30 mg/Kg) and Zn (99.40 mg/Kg) [30].

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Table 4. Concentration of Metals in Vegetable Samples Collected from the Farm .

Element	Vegetables					
	Spinach	Cabbage	Raddish	Tomatoes	Pepper	*RMLV
Cu	25.26±5.87	31.33±4.01	51.10±4.12	18.45±6.44	53.25±12.50	73.30
Mn	220.65±33.24	191.75±15.14	92.10±22.36	ND	29.85±8.35	500.00
Fe	103.00±88.44	85.00±30.11	93.55±33.56	77.63±35.22	80.69±38.77	425.50
Cd	3.25±0.12	0.71±0.02	5.70±0.55	ND	ND	0.20
Ni	13.00±0.15	ND	ND	ND	ND	67.90
Zn	53.77±22.11	33.54±4.02	0.89±0.05	ND	21.22±5.98	99.40
Pb	3.21±0.05	ND	ND	ND	ND	0.30

RMLV: Recommended Maximum Levels in Vegetables

*Source: [22 and 23]

Cabbage, bio-accumulated Cu, Mn, Fe, Cd and Zn from the soil and the concentrations of the metals were in the other Mn> Fe > Zn > Cu > Cd. The concentration of Cd in cabbage was also higher than the recommended maximum levels in vegetables (0.20mg/kg) [30]. This could be attributed to the urban solid waste used as manure in this farm. The other metals bio-accumulated in cabbage were also below the recommended maximum limits.

The results showed that radish in bio-accumulated only the metals Cu, Mn, Fe, Cr and Zn in its roots in the sequence Fe >Mn> Cu > Cr > Zn.The metals bio-accumulated were also below the recommended maximum limits for vegetables(see Tables 5).Tomatoeson the other hand bioaccumulated only Cu, Fe and Cd, in decreasing order of Fe > Cu > Cd.The concentration of Cd was also higher than the recommended maximum limit in vegetables.Pepper bio-accumulated Cu,

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Mn, Fe, Ni and Zn in the order Fe > Cu > Mn > Zn > Ni. The metals in pepper were within the recommended limit.

Generally, the concentration of iron was highest in almost all the vegetables. The higher concentration of Fe could be as a result of its oxygen carrier ability for chlorophyll production and also for protein synthesis [31]. The concentrations of Mn and Cu only were higher in cabbage than spinach. The results also showed that spinach, cabbage and radish, bioaccumulated more metals than pepper and tomato. This is in agreement with the reports of other researchers [24]. The higher levels of heavy metal contamination found in some fruit and vegetables could be closely related to the pollutants in irrigation water, farm soil, and pesticides or alternatively could be due to pollution from traffic on the highways [31].

Based on the pattern of metal accumulation in the vegetables, it could be suggested that radish and pepper could be safely grown on Cd contaminated soils. On the other hand, vegetables like spinach, cabbage, radish, may not suitable for cultivation on Cu, Mn, Fe, Zn and Cd contaminated soils. However, some fruit type vegetables like tomato and pepper could be safely grown on Cr, Ni, and Pb contaminated soils. Root type vegetable like radish could be cultivated on Cd, Cr, Ni and Pb contaminated soils. Heterogeneous accumulation of heavy metals in different crop species has been reported [7, 32], which could be attributed to their diverse morphological characteristics.

Conclusion

From this study, it could be concluded that the dumpsite was polluted with the metals Cu, Mn, Fe, Cd, Cr, Ni, Zn and Pb. The used of the dumpsite soil as manure, contaminated the farm studied. The concentration of the metals in the farm were in the order Fe > Mn > Cu > Zn > Ni > Cd > Pb. The vegetable grown in these farm bioaccumulated some of the metals analyzed. The differences in respect of metal uptake could be emphasized for selection of vegetable crops for

cultivation on metals contaminated soils depending on their metal uptake potential. The results of the Pearson correlation coefficient (r) showed perfect positive correlation values above 0.9 between the concentration of metals in the farm and the vegetables, which indicated that there was a strong association or similarity between them. At both $p < 0.05$ and $p < 0.01$ level of significant, all the correlations were significant. This implies that the similarity in the concentrations between the farm soil and vegetables were quite high.

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