

PHYTOAVAILABILITY AND FRACTIONATION OF CADMIUM AND LEAD IN VEGETABLE FARM SOILS IN ILORIN, NORTH-CENTRAL, NIGERIA

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ABSTRACT

Heavy metal dynamics, bioavailability and fractionation are of great importance to measure soil toxicity, remediation strategies and availability in soil. However, reports showed that not much has been done to evaluate these parameters in vegetable farm soils in Ilorin metropolis. These parameters aid in assessing risk potential and extent of heavy metal viability in soil. Therefore, soils were collected from major vegetable farms in Ilorin metropolis, sorted, air-dried, ground, and pretreated for further analysis. Thus, this study investigated the bioavailable Cd and Pb and their fractionation in vegetable farm soils in Ilorin metropolis. These experiments were conducted by single extraction procedure, sequential extraction and Atomic Absorption Spectrophotometry, alongside analysis of some key soil properties. The results showed that the soil pH ranged from 6.62 ± 0.04 to 7.18 ± 0.03 , organic matter $2.05 \pm 0.00\%$ to $3.50 \pm 0.005\%$ and cation exchangeable capacity 3.68 ± 0.02 cmolc/kg to 8.63 ± 0.03 cmolc/kg. The target heavy metals in the sampling areas were potentially bioavailable with phytoavailable concentration ranges of 0.00 ± 0.00 mg/kg to 0.67 ± 0.14 mg/kg for Cd and 0.33 ± 0.03 mg/kg to 6.25 ± 0.25 mg/kg for Pb. The target heavy metals showed a high viability of the soluble and exchangeable form in most soils and in both seasons which would greatly contribute to their availability to plant uptake and soil toxicity. There is also a threat of oxidization of the potentially available Cd and Pb in other forms due to pH ranges of most of the studied soils. Therefore, vegetable farm soils in Ilorin metropolis are polluted with Cd and Pb and may have high risk of causing human health problems when vegetables grown on the soils are consumed; which calls for remediation of most of the soils.

Keywords: Phytoavailability, Fractionation, Pollution, Heavy metal, Sequential extraction, Vegetable farm soils.

INTRODUCTION

Heavy metals abound naturally in soil environment, as a result of processes of weathering of parent materials at levels that are regarded as trace and rarely toxic substance, and also from human anthropogenic activities (Herawati *et al.*, 2010). Of the heavy metals that abound, cadmium (Cd) and lead (Pb) are common and widely studied contaminants because of their spectrum of use in production of lead-acid batteries, lead-based paints, automobiles, oil refineries, and antiknock in petrol (Ying *et al.*, 2013). In terms of environmental concentration, Pb is the heavy metal closest to the level in which toxic signs manifest than any other substance (Iwegbue *et al.*, 2013).

Heavy metal distribution, dynamics and transport in soil depend significantly on their chemical forms (Debnárová and Doleřa, 2010). Once in the soil, heavy metals are adsorbed by initial fast

reactions (minutes, hours), followed by slow adsorption reactions (days, years) and are, therefore, redistributed into different chemical forms with varying bioavailability, mobility and toxicity (Deng *et al.*, 2012).

Reports had shown that not all the heavy metals in the soil are readily available to plant but may become available under some environmental influences or changes such as pH, redox potential, cation exchange capacity, organic matter content and moisture content of the soil (Yadawe, 2011). The fraction of a total heavy metal content that is available for plant uptake in the soil depends strongly on the chemical form in which the metals are present (Lokeshwari and Chandrappa, 2012). Therefore, it is important to know the different forms of heavy metals in soil which will help in assessing the extent of toxicity or level of contaminations and remediation strategy of the heavy metal (Kabata-Pendias, 2004). The largest

form of the metals is bound to the soil solid form which is the form that controls the metal ion activity in the soil solution (Menzies *et al.*, 2007).

It has been established that the total concentrations of metals in soil do not provide information about metal phytoavailability. The chemical forms in which metals are present in soil determines the phytoavailability, mobility, and reactivity (Yadawe, 2011). The accurate estimation of heavy metal phytoavailability and fractionation in soils had been reported to be important risk assessment, remediation strategy and a measure its viability to plant (Kabata-Pendias, 2004). Heavy metal fractionation are the different chemical and physical forms of heavy metals in soil, which can be free ion or complexed to a ligand (Davidson *et al.*, 2006). It can be in the gaseous form, and distributed amongst solid phases within the soil (Manceau *et al.*, 2002).

There are five main chemical forms of heavy metals, and these are: exchangeable heavy metals which are the phytobioavailable or soluble fraction (F1), heavy metals bound to carbonate (F2), heavy metals bound to oxide (F3), heavy metals bound to organics fraction (F4) and residual heavy metals (F5) (Oluwatosin *et al.*, 2010). Heavy metals in soil are redistributed to different chemical forms with varying bioavailability, mobility and toxicity (Levy, 1992). Therefore, for a comprehensive description and understanding of phytoavailability of heavy metals in soils, there would be need to address all the various forms of a metal in soils (Haug, 2005).

Hence, assessment of phytoavailability and fractionation of heavy metals in agricultural soils becomes very essential in order to avoid pollution via food chain by heavy metals in soils (Haug *et al.*, 2005).

Zerbe *et al.* (1999) reported that Cd and Pb fractionations and their bioavailability in soil in the fractions of carbon-bound (F2) and oxides-bound (F3) contribute greatly to their availability to plant uptake (Forstner, 1993).

Therefore, vegetables grown on soils with elevated phytoavailable Cd and Pb stand the risks of being contaminated, and consumers of such vegetable stand the risk of picking up such

contaminants, which leads to health deterioration.

MATERIALS AND METHODS

Soil Sample Collection

Thirteen (13) selected top soils (0–15 cm) from the major vegetable farms in Ilorin metropolis were used. The soil of the University of Ilorin Botanical Garden was used as Control because literature has certified the concentrations of heavy metals of University of Ilorin Botanical Garden soil as suitable for Control with concentrations far below the WHO (2006) standard for agricultural soils.

Soils from sampling sites differ in physical and chemical properties and in the degrees of heavy metal contamination (Rayment and Higginson, 1992). Their textures ranged from sandy loam to clay with different anthropogenic activities around the sampling areas (Table 1).

Otte, Budo Egba, Mubo and Oyun sampling sites are located along the road. Sites of Coca Cola and Ola olu areas are located close to industrial layout, mechanic workshop and the road. Sites of Ojagboro and Isale Aluko are near major dumpsites while sites of Budo Abio and Odoore had low anthropogenic activities.

Sample collection was done both in the dry season (November, 2015 to February, 2016) and in the rainy season (August, 2016 to October, 2016) for this study.

Preparation and Characterization

Each soil sample was separately passed through a 10 mm sieve to remove large stones and grass debris, air-dried, ground, and passed through a 2 mm sieve for further laboratory analysis (AOAC, 2000).

The pH of each soil sample was measured in deionized water (1: 1, w/v) with a glass electrode using the method of Obrador *et al.* (2007). The organic matter (OM) content was determined via the Walkley-Black wet oxidation method of Reddy (2002). Cation exchange capacity (CEC) was determined using the ammonium acetate method (pH 7.0) according to the method of Rhoades *et al.* (1982).

Table 1: Description of the Sampling Sites in Ilorin, Nigeria and their GPS Coordinates

| S/NO | Sites | LOC | AA | ST | Latitude (N) | Longitude (E) | Altitude (Meters) |
|------|-----------------------|---------|---------------|----|--------------------|--------------------|-------------------|
| 1 | Otte | ATR | HVE:MAA | L | 8° 31 ¹ | 4° 39 ¹ | 347.0 |
| 2 | Budo Egba | ATR | HVE:LAA | LS | 8° 32 ¹ | 4° 39 ¹ | 346.6 |
| 3 | Budo Abio | BTN | LAA | L | 8° 30 ¹ | 4° 53 ¹ | 365.0 |
| 4 | Mubo | WTN:ATR | DW:HVE:HDS | L | 8° 50 ¹ | 4° 70 ¹ | 270.4 |
| 5 | Oyun | ATR | VHE:HDW | L | 8° 53 ¹ | 4° 60 ¹ | 284.5 |
| 6 | Ojagboro | BTN | HD:HDW | L | 8° 15 ¹ | 4° 57 ¹ | 262.2 |
| 7 | Olaolu | ATH: IA | HVE: HIW | LS | 8° 47 ¹ | 4° 57 ¹ | 282.7 |
| 8 | Eroomo | WTN | MAA | LS | 8° 45 ¹ | 4° 58 ¹ | 327.1 |
| 9 | Okeodo | ATR | HVE: MDS | LS | 8° 47 ¹ | 4° 64 ¹ | 332.8 |
| 10 | Cocacola | IA: ATR | HIW: HVE: HDS | LS | 8° 47 ¹ | 4° 56 ¹ | 265.5 |
| 11 | Isale Aluko | WTN | HDS:HDW:HDS | L | 8° 49 ¹ | 4° 54 ¹ | 302.9 |
| 12 | Odoore | BTN | LAA | L | 8° 43 ¹ | 4° 50 ¹ | 354.1 |
| 13 | Botanical garden (CS) | OTR | LAA | L | 8° 47 ¹ | 4° 66 ¹ | 290.9 |

Abbreviations: LGA - Local Government Area, N-North of the Equator, E-East of the Greenwich Meridian, CS- Control Site, LOC- Location, ATR-Along the Road, IA- Industrial Area, HIW- Heavy Industrial Waste, WTN- Within The Neighborhood, BTN- Behind The Neighborhood, OTR- Off The Road, LVE- Low Vehicular Emission, MVE-Moderate Vehicular Emission, HVE- Heavy Vehicular Emission, AA-Anthropogenic Activities, LAA- Low Anthropogenic Activities, MAA- Moderate Anthropogenic Activities, MDS-Moderate Dump Site, HDS-Heavy Dump Site, HDW- Heavy Domestic Waste, ST- Soil Texture, L- Loam, LS- Loam Sandy.

**Figure 1:** Map of Ilorin Metropolis, Kwara State, Nigeria, Showing the Sampling Sites

Single Extraction Procedure for Phytoavailability of Heavy Metals.

Phytoavailable heavy metal analysis of the soil samples were done using single extraction procedure of Tessier *et al.* (1979) and Song *et al.* (2008). One (1) g each of the air-dried pre-sieved composite top soil sample was weighed into a 100 ml volumetric flask. It was extracted at room temperature with 8 ml of magnesium chloride solution (0.5 M MgCl₂) by continuous agitation at pH 7 for 20 mins. Extracted solution and the blank (MgCl₂) were filtered using Whatman No 42 filter

paper and <0.45 μm Millipore filter paper. Each filtrate was transferred into a 25 ml volumetric bottle and made up to the mark with distilled water. Phytoavailable contents of Cd and Pb in the soil filtrates were analyzed using Perkin Elmer 200 Analyst Spectrophotometer (AAS).

Tessier's Sequential Extraction for Cd and Pb Fractionation

The different forms of Cd and Pb in soils were determined using the method of Tessier *et al.* (1979) and Joksic (2005). Exchangeable heavy

metal fractions were extracted in 20 ml of NH_4NO_3 solution. The heavy metals bound to carbonate fraction were extracted in 16 ml of 1 M sodium acetate/acetic acid buffer at pH 5 for 5 hours at room temperature. Heavy metals bound to oxide fraction were extracted in 13.9 g of hydroxyl amine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) dissolved in 500 ml of distilled water (0.4 M $\text{NH}_2\text{OH}\cdot\text{HCl}$). Heavy metals bound to organic fraction were extracted in 3 ml of 0.02M HNO_3 and 5 ml of 30% (v/v) hydrogen peroxide while the residual heavy metals fraction were extracted in 5 ml conc. HNO_3 (HNO_3 , 70% w/w), 10 ml of hydrofluoric acid (HF, 40% w/w) and 10 ml of perchloric acid (HClO_4 , 60% w/w) in Teflon beakers.

The forms of heavy metals in each extract were determined using PerkinElmer 200 Analyst Spectrophotometer (AAS). The procedure was validated and the instrument calibrated. Blanks were prepared for correction of background and other sources of error. The results of the sequential extraction were checked by summing up the different concentrations of fractions for each element and compared with the results obtained from the total heavy metals in the soils

Statistical Analysis

The means and standard deviations (SD) were calculated using Excel (Microsoft Inc.) software packages. One-way analysis of variance (ANOVA) was carried out with SPSS16.0. The statistical difference ($p < 0.05$) observed between samples and multiple comparisons were made by Duncan multiple range test.

RESULTS AND DISCUSSION

Tables 2 and 3 showed the results of the selected soil properties and the phytoavailable target heavy metal concentrations (extractable fractions) in both dry and rainy seasons.

The results showed that the soils used for this study varied widely in their properties, there was significant difference in the mean content of physicochemical properties (pH, organic matter content (OM) and cation exchangeable capacity (CEC)) and the phytoavailable heavy metals in soils of the study sites in both seasons at $p \leq 0.05$.

The soil pH of study sites ranged from slightly acidic to slightly alkaline with the range of 6.62 ± 0.04 and 7.18 ± 0.03 during the dry season while the range was 6.59 ± 0.08 and 6.97 ± 0.19 during the rainy season.

All soils were characterized by low and medium organic carbon contents ranging from $2.09 \pm 0.01\%$ to $3.50 \pm 0.05\%$ during the dry season while in the rainy season it ranged from $2.24 \pm 0.11\%$ to $3.01 \pm 0.20\%$. The cation exchangeable capacity (CEC) in the dry season ranged from $3.68 \pm 0.02 \text{ cmol}_c \text{ kg}^{-1}$ to $8.63 \pm 0.03 \text{ cmol}_c \text{ kg}^{-1}$ while in the rainy season it ranged from $4.61 \pm 0.71 \text{ cmol}_c \text{ kg}^{-1}$ to $6.09 \pm 1.11 \text{ cmol}_c \text{ kg}^{-1}$. Soil of Mubo had the highest values of pH and organic matter in the dry season, which was higher than the value obtained in the rainy season.

All the soils from the study sites had pH and organic carbon range between the WHO/EU (2006) permissible limit for agriculture soils. The soil pH (5.5 -7.5) and organic matter content (1%-6%) in both seasons had higher values in the dry season than in the rainy season.

Soil of Odoore had the highest CEC than all the other soils in the dry season. This indicated more clay and organic matter in the soil, hence, greater water holding capacity and more fertility than soils of the other sites. The phytoavailable target heavy metals of vegetable soils in Ilorin metropolis in the dry season showed that there was significant difference between the Control soil and all the other soils at $P < 0.05$. The study indicated that the phytoavailable heavy metals in the soils varied significantly among sites and between seasons as shown by earlier study of Atayese *et al.* (2009).

It was also revealed in this study that Cd was more phytoavailable in the dry season than in the rainy season. This is consistent with the findings of Ashraf *et al.* (2012), and it could be attributed to the pH range and the cation exchange capacity of the soil supporting Cd complexation in the dry season than in the rainy season. The lowest phytoavailable Cd was obtained for the Control soil, which could be due to low pollution from agricultural practices or anthropogenic activities.

It was shown in this study that mostly all soils

showed elevated levels of phytoavailable cadmium and lead in the dry season except for soil of the Eroomo, Odoore and the Control site while lead was more phytoavailable in the rainy season than cadmium. The reason could be due to seasonal variation which could have been supported by the soil physicochemical properties like the pH, soil organic matter and the cation exchange capacity of the soil which corroborates the submission of Yadawe (2011). Mostly all the soils of the study sites stand the risk of pollution by Cd and Pb most especially in the dry season with most values above the WHO (2006) permissible value of phytoavailable Cd of 0.3mg/kg.

Therefore, the result showed that extractable portion or the phytoavailable form of Cd (0.11 ± 0.0 mg/kg to 0.67 ± 0.14 mg/kg) in most of the sites were greater than the permissible limit of Cd while the soluble portion of lead (Pb) in soils in both seasons were between 0.33 ± 0.03 mg/kg and 6.25 ± 0.25 mg/kg. The result indicated Cd and Pb pollution in the soils of these sites which is an indication that most of the soils need to be remediated for planting.

The result also indicated strong relationship between the phytoavailable heavy metal concentrations and soil properties (Tables 2 and 3) which agrees with findings of Zurera *et al.* (1989).

Table 2: Physicochemical Properties, Phytoavailable Cd and Pb (mg/kg) in Vegetable Farm Soils at some Sites in Ilorin, Nigeria during Dry Season

| Site | pH | OM% | CEC cmocl kg ⁻¹ | Cd | Pb |
|-----------------|-------------------------|------------------------|-------------------------------|--------------------------|--------------------------|
| Otte | 6.93±0.1 ^c | 2.23±0.01 ⁱ | 6.51±0.09 ^{bc} | 0.42±0.02 ^{bcd} | 0.83±0.14 ^{fg} |
| Budo Egba | 6.62±0.04 ^b | 3.07±0.02 ^c | 5.56±0.01 ^c | 0.50±0.00 ^b | 1.33±0.31 ^{efg} |
| Budo Abio | 6.88±0.01 ^d | 2.47±0.05 ^g | 5.04±0.03 ^h | 0.33±0.02 ^{cd} | 1.92±0.40 ^{ef} |
| Mubo | 7.18±0.03 ^a | 3.50±0.05 ^a | 5.93±0.04 ^{cd} | 0.50±0.03 ^b | 1.92±0.11 ^{ef} |
| Oyun | 7.05±0.04 ^b | 3.20±0.02 ^b | 5.43±0.02 ^f | 0.42±0.03 ^{bcd} | 2.92±0.27 ^{de} |
| Ojagboro | 6.81±0.01 ^f | 2.77±0.02 ^c | 5.21±0.03 ^g | 0.45±0.08 ^{bcd} | 5.17±0.20 ^{ab} |
| Olaolu | 6.69±0.01 ^f | 2.46±0.03 ^g | 4.05±0.01 ^j | 0.25±0.05 ^d | 4.37±0.40 ^b |
| Eroomo | 6.63±0.04 ^{hg} | 2.53±0.02 ^f | 5.89±0.01 ^d | 0.17±0.03 ^{de} | 3.17±0.11 ^{cde} |
| Okeodo | 6.85±0.01 ^c | 2.97±0.04 ^d | 6.55±0.01 ^b | 0.25±0.00 ^d | 3.75±0.78 ^{cd} |
| Coca cola | 7.08±0.04 ^b | 2.05±0.02 ^j | 5.84±0.06 ^d | 0.67±0.14 ^a | 5.83±0.46 ^a |
| IsaleAluko | 6.94±0.01 ^c | 2.36±0.02 ^h | 3.68±0.02 ^k | 0.53±0.04 ^b | 1.50±0.18 ^{fg} |
| Odoore | 6.68±0.01 ^f | 2.09±0.01 ^j | 8.63±0.03 ^a | 0.14±0.03 ^a | 0.92±0.16 ^f |
| Bot.garden (CS) | 6.67±0.01 ^{fg} | 2.56±0.03 ^f | 4.83±0.03 ⁱ | 0.11±0.02 ^c | 0.50±0.07 ^h |

Mean value with same alphabet along the same column are significantly the same at $p \leq 0.05$ using Duncan Multiple Range Test, CS: Control Site, OM: Organic matter, CEC: Cation Exchangeable Capacity. WHO (2006) safe limit of Cd=0.03 mg/kg and Pb = 2.00 mg/kg.

Table 3: Physicochemical Properties, Phytoavailable Cd and Pb (mg/kg) in Vegetable Farm Soils at some Sites in Ilorin, Nigeria during Rainy Season

| Site | Ph | OM % | CEC cmolc kg ⁻¹ | Cd | Pb |
|-----------------------|-------------------------|-------------------------|-------------------------------|------------------------|--------------------------|
| Otte | 6.91±0.16 ^{ab} | 3.01±0.20 ^a | 6.01±0.80 ^{ab} | 0.08±0.04 ^a | 4.08±0.12 ^{bc} |
| Budo Egba | 6.97±0.19 ^a | 2.65±0.50 ^{bc} | 5.86±0.68 ^b | 0.08±0.02 ^a | 4.27±0.03 ^{ab} |
| Budo Abio | 6.88±0.16 ^{ab} | 2.45±0.48 ^d | 5.90±0.61 ^b | 0.00±0.00 ^b | 0.68±0.12 ^c |
| Mubo | 6.77±0.23 ^{ab} | 2.37±0.41 ^{dc} | 5.67±0.27 ^b | 0.08±0.00 ^a | 4.30±0.29 ^{ab} |
| Oyun | 6.75±0.05 ^{ab} | 2.41±0.27 ^d | 6.09±1.11 ^a | 0.08±0.11 ^a | 3.97±0.63 ^{abc} |
| Ojagboro | 6.70±0.17 ^{ab} | 2.37±0.16 ^d | 5.60±1.80 ^b | 0.08±0.03 ^a | 2.33±0.12 ^c |
| Olaolu | 6.71±0.13 ^{ab} | 2.31±0.14 ^d | 5.45±1.84 ^{bc} | 0.08±0.03 ^a | 3.58±0.02 ^b |
| Eroomo | 6.59±0.08 ^b | 2.28±0.22 ^e | 4.61±0.71 ^c | 0.00±0.00 ^c | 0.65±0.36 ^{ij} |
| Okeodo | 6.60±0.06 ^b | 2.24±0.11 ^e | 5.31±0.19 ^{bc} | 0.08±0.11 ^a | 2.42±0.38 ^c |
| Coca cola | 6.72±0.28 ^{ab} | 2.48±0.55 ^{cd} | 5.33±0.31 ^{bc} | 0.08±0.14 ^a | 6.25±0.25 ^a |
| IsaleAluko | 6.86±0.26 ^{ab} | 2.57±0.44 ^c | 5.16±0.58 ^{bc} | 0.08±0.11 ^a | 1.82±0.38 ^d |
| Odoore | 6.92±0.15 ^{ab} | 2.75±0.48 ^b | 5.51±0.92 ^b | 0.00±0.00 ^b | 0.44±0.12 ^{ef} |
| Botanical garden (CS) | 6.93±0.18 ^{ab} | 2.84±0.47 ^{ab} | 5.31±0.99 ^b | 0.00±0.00 ^b | 0.33±0.03 ^f |

Mean value with same alphabet along the same column are significantly the same at $p \leq 0.05$ using Duncan Multiple Range Test, CS: Control Site, OM: Organic carbon, CEC=Cation Exchangeable Capacity. WHO (2006) safe limit of Cd=0.03 mg/kg and Pb = 2.00 mg/kg.

Tables 4-5 showed that Cd fractionation in soil varied significantly among sites and between seasons supporting the study of Diaz-de Alba *et al.* (2011). There was significant difference in the fractions of cadmium between the sites and seasons at $p \leq 0.05$. The fraction of cadmium (Cd) in the exchangeable (F1), bound to carbonate (F2) and residual forms (F5) were more in the soil in dry season indicating more soluble or labile Cd in soil in dry season, while the oxide (F3) and organic (F4) forms of Cd were more in the rainy season. Low amount of Cd bound to residual fraction compared with that in other geochemical phases indicated higher mobility of the metal in the soil. Similar result was reported in another related study (Ashraf *et al.*, 2012). This showed that Cd would easily be released to the soil and highly toxic under favorable conditions like pH, organic matter, cation exchangeable capacity and electrical conductivity.

Soils of Otte and Budo Egba had more of the exchangeable Cd than the soils from other sites. Soil of the Control soil recorded zero value for all the forms of Cd except the Cd bound to residual fraction. The Cd residual fraction in the Control soil could be due to geogenic origin and complexation of Cd with the soil sediments being released after degradation of organic matter

which corroborates the study of Cabral and Lefebvre (1998). The soluble and exchangeable heavy metal form of Cd usually considered as most hazardous (Maiz *et al.*, 2000), were more in the dry season than in the rainy season. This is similar to the report of Gupta *et al.* (2005) that got more soluble fraction of cadmium in the dry season than in the rainy season.

This could be due to the low soil pH and cation exchange capacity in the dry season than in the rainy season that supported Cd mobility and dynamic in soil which would likely render the soils more polluted by Cd. Tables 6 and 7 showed significant differences in the fractionation of Pb in both seasons. Lead was more bound to carbonate (F2), oxide (F3) and organics (F4) in the soil in the dry season unlike Cd, while Pb in the rainy season was more in the forms of exchangeable (F1) and residual fraction. Soils of Otte, Olaolu, Okeodo and Isale Aluko recorded higher exchangeable Pb than soils of the other sites in the dry season. The soils of the Control site in the rainy season were more contaminated with Pb than in the dry season with Pb bound to carbonate, oxides and organics in the soils. The results suggested that Cd and Pb fractionation in the soils varies with season which can be due to difference in the physico-chemical properties of

soils such as pH, organic matter, cation exchangeable capacity, electrical conductivity, soil moisture, bulk density and clay matter.

The soils of some sites such as Otte, Budo Egba, Olaolu, Okeodo, Coca Cola and Isale Aluko were contaminated with both Cd and Pb. This could be due to the activities around the sampling areas such as agricultural activities, proximity to the road, thereby receiving vehicular emission, exhausts from mechanic workshops, industrial discharge and solid wastes of dumpsite. The result

showed that the resultant difference in the wastes were sources of heavy metals from activities from those areas which could lead to complexation of heavy metals with sediments being released after oxidation of sulphides from wastes to sulphates. The oxidized complexes are weakly bound and are readily available in soil at suitable environmental conditions (Diaz-de Alba *et al.*, 2011). There was an indication that fractions of Cd and Pb in the soils of the sampling sites are directly related to their solubility which controls its mobility as reported by Xian (1989).

Table 4: Fractionation of Cd (mg/kg) in the Vegetable Farm Soils at some Sites in Ilorin, Nigeria during Dry Season

| Sites | Exchangeable Fraction | BT Carbon Fraction | BT Oxides Fraction | BT Organic Fraction | Residual Cd/ Inert Fraction |
|----------------------|-------------------------|-------------------------|-------------------------|-------------------------|-----------------------------|
| Otte | 1.33±0.00 ^b | 0.33±0.00 ^d | 0.67±0.00 ^a | 0.67±0.00 ^{ab} | 0.67±0.00 ^{bc} |
| Budo Egba | 1.67±0.00 ^a | 1.00±0.00 ^b | 0.60±0.00 ^{ab} | 0.56±0.19 ^{bc} | 0.40±0.19 ^{cd} |
| Budo Abio | 0.22±0.19 ^{de} | 0.33±0.00 ^d | 0.00±0.00 ^e | 0.22±0.19 ^{de} | 0.22±0.00 ^e |
| Mubo | 0.33±0.00 ^d | 1.00±0.00 ^b | 0.56±0.51 ^b | 0.89±0.39 ^a | 1.11±0.39 ^a |
| Oyun | 0.33±0.00 ^d | 0.67±0.00 ^c | 0.22±0.35 ^{cd} | 0.44±0.38 ^c | 0.33±0.58 ^d |
| Oja gboro | 0.67±0.00 ^c | 0.67±0.00 ^c | 0.33±0.00 ^c | 0.33±0.57 ^d | 0.67±0.58 ^{bc} |
| Olaolu | 0.67±0.00 ^c | 0.67±0.00 ^c | 0.22±0.19 ^{cd} | 0.67±0.58 ^{ab} | 1.00±0.58 ^b |
| Eroomo | 0.33±0.00 ^d | 0.00±0.00 ^e | 0.11±0.19 ^d | 0.44±0.19 ^c | 0.56±0.19 ^c |
| Okeodo | 0.67±0.00 ^c | 1.33±0.00 ^a | 0.22±0.35 ^{cd} | 0.22±0.39 ^{de} | 0.44±0.39 ^{cd} |
| Coca cola | 0.67±0.58 ^c | 0.57±0.51 ^{cd} | 0.33±0.00 ^c | 0.56±0.19 ^{bc} | 0.44±0.39 ^{cd} |
| Isale Aluko | 0.33±0.00 ^d | 0.22±0.19 ^d | 0.44±0.77 ^{bc} | 0.56±0.39 ^{bc} | 0.38±0.58 ^d |
| Odoore | 0.19±0.11 ^{de} | 0.00±0.00 ^e | 0.00±0.00 ^e | 0.67±0.58 ^{ab} | 0.22±0.39 ^e |
| Botanical garden(CS) | 0.00±0.00 ^e | 0.00±0.00 ^e | 0.00±0.00 ^e | 0.00±0.00 ^f | 0.11±0.19 ^f |

Mean value with same alphabet along the same column are statistically the same at $p \leq 0.05$ using Duncan Multiple Range Test, CS: Control Site, BT: Bound To. Values represent mean \pm SD.

Table 5: Fractionation of Cd (mg/kg) in the Vegetable Farm Soils at some Sites in Ilorin, Nigeria during Rainy Season

| Site | Exchangeable Cd | BT Carbon fraction | BT Oxides Fraction | BT Organics Fraction | Residual/Inert Cd fraction |
|-----------------------|------------------------|------------------------|------------------------|------------------------|----------------------------|
| Otte | 0.25±0.00 ^a | 1.17±0.10 ^a | 1.08±0.12 ^a | 0.58±0.14 ^a | 0.22±0.09 ^b |
| Budo Egba | 0.25±0.00 ^a | 1.17±0.14 ^a | 0.68±0.12 ^b | 0.33±0.04 ^b | 0.27±0.09 ^a |
| Budo Abio | 0.00±0.00 ^c | 0.33±0.12 ^c | 0.08±0.14 ^c | 0.17±0.13 ^d | 0.22±0.09 ^b |
| Mubo | 0.00±0.00 ^c | 0.17±0.14 ^a | 0.25±0.00 ^c | 0.33±0.14 ^b | 0.17±0.17 ^c |
| Oyun | 0.00±0.00 ^c | 0.08±0.14 ^d | 0.17±0.14 ^d | 0.25±0.00 ^c | 0.11±0.10 ^f |
| Ojagboro | 0.25±0.00 ^a | 0.08±0.12 ^d | 0.17±0.14 ^d | 0.17±0.28 ^d | 0.00±0.00 ^d |
| Olaolu | 0.08±0.14 ^b | 0.08±0.14 ^d | 0.17±0.29 ^d | 0.08±0.14 ^c | 0.06±0.10 ^e |
| Eroomo | 0.00±0.00 ^c | 0.08±0.14 ^d | 0.17±0.14 ^d | 0.17±0.10 ^d | 0.06±0.10 ^e |
| Okeodo | 0.00±0.00 ^c | 0.08±0.14 ^d | 0.17±0.14 ^d | 0.08±0.14 ^c | 0.06±0.10 ^e |
| Cocacola | 0.25±0.00 ^a | 0.08±0.14 ^d | 0.08±0.14 ^c | 0.08±0.14 ^c | 0.11±0.10 ^c |
| Isale Aluko | 0.25±0.00 ^a | 0.08±0.14 ^d | 0.17±0.14 ^d | 0.17±0.14 ^d | 0.06±0.10 ^e |
| Odoore | 0.00±0.00 ^c | 0.08±0.14 ^b | 0.08±0.14 ^c | 0.08±0.14 ^c | 0.05±0.10 ^e |
| Botanical Garden (CS) | 0.00±0.00 ^c | 0.00±0.00 ^e | 0.00±0.00 ^e | 0.00±0.00 ^f | 0.00±0.00 ^f |

Mean value with same alphabet along the same column are statistically the same at $p \leq 0.05$ using Duncan Multiple Range Test, CS: Control Site, BT: Bound To. Values represent mean \pm SD.

Table 6: Fractionation of Pb (mg/kg) in the Vegetable Farm Soils at some Sites in Ilorin, Nigeria during Dry Season

| Sites | Exchangeable Fraction | BT Carbon Fraction | BT Oxides Fraction | BT Organics Fraction | Residuals/ Inert Fraction |
|----------------------|------------------------|------------------------|-------------------------|--------------------------|---------------------------|
| Otte | 0.67±0.14 ^a | 2.85±0.00 ^c | 2.33±0.00 ^d | 1.31±0.00 ^b | 3.33±0.00 ^c |
| Budo Egba | 0.33±0.11 ^c | 2.73±0.00 ^d | 2.10±0.09 ^{de} | 1.30±0.00 ^{def} | 4.00±0.00 ^b |
| Budo Abio | 0.00±0.00 ^e | 0.83±0.00 ^g | 0.33±0.10 ^g | 1.46±0.00 ^b | 0.41±0.00 ^{gh} |
| Mubo | 0.17±0.00 ^d | 3.00±0.00 ^b | 0.43±0.00 ^{fg} | 4.00±0.00 ^b | 1.67±0.00 ^d |
| Oyun | 0.33±0.07 ^c | 3.33±0.09 ^b | 0.67±0.39 ^{ef} | 4.00±0.00 ^b | 1.00±0.00 ^e |
| Ojagboro | 0.00±0.00 ^e | 3.00±0.11 ^b | 5.25±0.25 ^{ab} | 3.00±0.10 ^c | 5.00±0.00 ^a |
| Olaolu | 0.67±0.11 ^a | 5.00±0.00 ^a | 4.33±0.00 ^b | 1.33±0.00 ^{def} | 3.00±0.00 ^c |
| Eroomo | 0.00±0.00 ^e | 1.33±0.00 ^e | 0.41±0.19 ^{fg} | 1.67±0.00 ^d | 4.15±0.00 ^b |
| Okeodo | 0.67±0.11 ^a | 2.70±0.00 ^a | 3.77±0.29 ^c | 2.25±0.25 ^{cd} | 0.50±0.00 ^{fg} |
| Coca cola | 0.33±0.00 ^c | 2.33±0.00 ^d | 1.03±0.09 ^e | 4.20±0.58 ^b | 0.67±0.00 ^f |
| IsaleAluko | 0.58±0.14 ^b | 0.67±0.11 ^f | 5.33±0.21 ^a | 7.33±0.39 ^a | 1.10±0.00 ^e |
| Odoore | 0.00±0.00 ^e | 0.00±0.00 ^g | 0.17±0.19 ^{gh} | 1.00±0.29 ^{ef} | 0.57±0.00 ^{fg} |
| Botanical Garden(CS) | 0.00±0.00 ^e | 0.00±0.00 ^g | 0.00±0.00 ^h | 0.33±0.17 ^f | 0.30±0.00 ^h |

Mean value with same alphabet along the same column are statistically the same at $p \leq 0.05$ using Duncan Multiple Range Test, CS: Control Site, BT: Bound To. Values represent mean \pm SD.

Table 7: Fractionation of Pb (mg/kg) in the Vegetable Farm Soils at some Sites in Ilorin, Nigeria during Rainy Season

| Site | Exchangeable Fraction | BT Carbon Fraction | BT Oxides Fraction | BT Organics Fraction | Residual/Inert Fraction |
|-----------------------|-------------------------|-------------------------|-------------------------|--------------------------|--------------------------|
| Otte | 8.00±0.00 ^c | 8.50±0.25 ^c | 7.25±0.25 ^c | 4.25±0.25 ^{cd} | 0.79±0.26 ^{cd} |
| Budo Egba | 7.08±0.12 ^f | 7.14±0.13 ^{de} | 6.00±0.10 ^{de} | 2.83±0.38 ^{de} | 0.39±0.10 ^{ef} |
| Budo Abio | 4.08±0.12 ^g | 0.83±0.12 ^g | 3.50±0.26 ^g | 1.42±0.08 ^g | 0.28±0.09 ^f |
| Mubo | 1.25±0.25 ^h | 0.50±0.25 ^h | 1.92±0.13 ^h | 0.75±0.25 ^{hi} | 0.84±0.89 ^c |
| Oyun | 9.00±0.25 ^d | 8.30±0.42 ^{cd} | 8.92±0.63 ^b | 1.00±0.25 ^h | 0.40±0.20 ^{ef} |
| Ojagboro | 9.92±0.52 ^c | 4.33±0.12 ^{ef} | 6.08±0.12 ^{de} | 4.67±0.13 ^c | 0.33±0.00 ^{efg} |
| Olaolu | 10.83±0.63 ^b | 18.33±0.72 ^a | 7.33±0.14 ^{bc} | 5.25±0.50 ^b | 1.57±0.63 ^a |
| Eroomo | 6.58±0.12 ^{fg} | 7.67±0.13 ^d | 4.33±0.13 ^{fg} | 2.33±0.12 ^{efg} | 0.64±0.19 ^d |
| Okeodo | 8.58±0.12 ^{de} | 8.25±0.00 ^{cd} | 4.58±0.12 ^f | 2.50±0.00 ^{ef} | 0.45±0.16 ^e |
| Cocacola | 11.33±0.29 ^a | 9.58±0.12 ^b | 5.50±0.25 ^c | 2.42±0.14 ^{ef} | 0.35±0.10 ^{efg} |
| Isale Aluko | 8.00±0.25 ^e | 9.42±0.13 ^{bc} | 9.67±0.13 ^a | 5.58±0.14 ^a | 0.91±0.10 ^b |
| Odoore | 6.50±0.25 ^{fg} | 4.67±0.13 ^e | 6.50±0.00 ^d | 3.08±0.02 ^d | 0.58±0.26 ^{de} |
| Botanical Garden (CS) | 0.92±0.08 ⁱ | 2.17±0.13 ^f | 1.83±0.38 ^{hi} | 1.33±0.14 ^{gh} | 0.22±0.09 ^{fg} |

Mean value with same alphabet along the same column are statistically the same at $p \leq 0.05$ using Duncan Multiple Range Test, CS: Control Site, BT: Bound To. Values represent mean \pm SD.

CONCLUSION

The study is an important risk assessment tool, remediation guide and a measure of heavy metal availability in the soils of vegetable farms in Ilorin, Nigeria. It is indicated in the results that most soils in Ilorin, Kwara State used for growing vegetables need remediation or the use should be discontinued for growing vegetables. The study further enunciates that soils for agricultural

purposes should be well protected to prevent contamination by heavy metals.

It is hereby recommended that soils for growing vegetables should be continuously monitored to ensure that concentration of readily available forms or fractions of cadmium (Cd) and lead (Pb) are maintained below the permissible limit to avoid phytoabsorption.

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