

Soil Metal Distribution under Different Land Uses of Emerging Mega Cities in Southwest Nigeria and the Associated Ecological Risk

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Abstract

Data on Inventory, distribution and risk assessment of heavy metals in soils of emerging megacities in sub-Saharan African countries is necessary to assess pollution sources and environmental safety. The present study evaluated Ni, Cr, Cu, Cd, Zn, Mn, and Pb concentrations in soils from different land uses in Ibadan and Abeokuta, Nigeria. Samples were collected at 0-20 and 20-40cm depths from crop-farm, industrial site, animal-farm, natural forest, roadside, educational institution, residential estate and markets. Results showed that the depth distribution of the metals were similar, Cu and Pb were concentrated in the top 20cm soil depth at both locations. There were higher concentrations of Ni, Cu and Zn in Ibadan soils while Abeokuta had higher levels of Mn. Copper and Zn contamination were higher in animal farm and industrial land, respectively. Roadside soil had a significantly higher Pb ($p < 0.05$), comparable to forest, educational and residential lands; however, market land use was more acidic. The soil metals accumulated and appeared bound to organic matter, while nickel was positive and significantly correlated with soil Cr, Cu, Zn and Mn while soil Zn and Mn correlated positively with Cr. Contamination/pollution factor across soil depth, locations and land use was in the order $Cd > Zn > Mn > Cr > Pb > Cu > Ni$. The soils' contamination indices are high with Cd, moderate with Zn and low for other metals. Cadmium has a high potential ecological risk, while the potential ecological risk indices of the locations were moderate. Generally, the metal concentrations were lower than those of other developed megacities.

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Keywords: Alfisols, Ecological risk, Heavy metals, Land use, Soil contamination, Urban soils.

1. Introduction

The soil is a repository of contaminants and of importance in ecosystems research (Luo *et al.*, 2007) and pollution studies (Madrid *et al.*, 2002). Among the components of the environment (soil, water, air), soil receives most of its pollutants from other components of the environment. Urban soils however, have high concentrations of heavy metals (Xia *et al.*, 2011; Adedeji *et al.*, 2013). Soils from urban areas are not usually used for farming. This is because of other high valued alternative uses to which the land are used for. However, alternative anthropogenic activities on urban soils have impacted high metals input in the soil, usually above permissible limits. Some of the pathways of exposure to soil contaminants are the inhalation and swallowing of pollutants, and at times, there is dermal contact with the pollutants (Nicholson *et al.*, 2003). This has resulted in toxicological health disorders in adults and children, affecting the central nervous systems and fatty tissues (Xia *et al.*, 2011).

Sources of pollution in urban soils are many and at times metal specific. Soil pollutants could have their sources from vehicle emission, chemical industry, coal combustion, municipal solid waste, drug contamination and dust sedimentation (Adedeji *et al.*, 2013; Azeez *et al.*, 2014; Jalili and Azizkhan, 2009; Xia *et al.*, 2011). For example, the concentrations of Cu, Pb and Zn are reported to be via traffic sources while most Cd sources are industrial (Imperato *et al.*, 2003; Xia *et al.*, 2011).

Other identified sources of soil heavy metals include agricultural inputs (Huang and Jin, 2008), urbanization, industrialization, and mining (Zhong *et al.*, 2012). Agricultural and industrial wastes are reported to be the most damaging anthropogenic activities in the world (Krami *et al.*, 2013). Several studies have also credited heavy metals pollution to anthropogenic sources (Zhang *et al.*, 2009; Acosta *et al.*, 2011; Bini *et al.*, 2011; Gu *et al.*, 2012; Li and Feng, 2012; Chabukdhara and Nema, 2012; Cai *et al.*, 2012; Guo *et al.*, 2012). Despite the negative effects (toxic effects) of these metals in human, their build-up in the soil is not properly monitored in emerging megacities of sub-Saharan Africa. Aside been present in the soils, these metals can also persist for a long time because they are not biodegradable and are immobile. The metals have been reported to be responsible for chronic and acute health disorders in adults and children (Madrid *et al.*, 2002; Lee *et al.*, 2006).

Human activities have been reported to affect the natural, geological and biological redistribution of heavy metals in soils (Peter and Adeniyi, 2011). Such activities in urban areas have contributed to the high metal profiles. Recently, research attention has focused on contamination of soils in urban cities in developed countries of Europe, America and Asia. Many of these studies have focused on urban soils as a part of the environment but not on specific land use types. This indicates a research gap, this aspect of research is, however,

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important because different land-use exert different pollution pressures on the land, and the changes in the environmental chemistry, particularly of heavy metals is also dependent on anthropogenic impact on the environment. The toxicological health risks associated with the land use also differs. Thus, information on soil distribution of heavy metals is necessary to assess soil specific pollution sources and soil quality (Gu *et al.*, 2012). This approach will allow for the evaluation of the potential risk of pollutants to other organisms and the potential impact on human.

Abeokuta and Ibadan (capitals of Ogun and Oyo states, respectively) are representative towns of southwestern Nigeria by human population, activities and geographical location. They are emerging megacities that border Lagos State, the most populous and commercial capital of Nigeria. The two cities in recent times have become foreign investor's destination of choice and emerging commercial hub in southwestern Nigeria. The two cities are old with a constantly growing population. Ibadan (with 11 local governments) has a population estimate of 3.6 million while Abeokuta (comprising of Abeokuta north and south, Odeda, Ifo and Ewekoro local governments) has a population of about 1.2 million inhabitants in 2006 national population census. Their nearness to Lagos has attracted several residents to the cities. These high populations have resulted into increase in human activities and the attendant problems of soil pollution. In the developed world, several studies have been reported on the heavy metal concentrations in urban and suburban soils (Xia *et al.*, 2011; Zheng *et al.*, 2008; DEFRA, 2009) of China, Netherlands, United Kingdom and Spain (Adriano, 2001) but only few in Nigeria have been reported in literature (Peter and Adeniyi, 2011; Bolaji *et al.*, 2009; Atayese *et al.*, 2008; Iwegbue, 2014; Iwegbue *et al.*, 2012; Iwegbue *et al.*, 2015). Specifically, there are scanty published researches on the concentrations of heavy metals in different land use in sub-Saharan Africa and particularly southwestern Nigeria except those related researches on Lagos State, Nigeria (Peter and Adeniyi, 2011; Bolaji *et al.*, 2009). The present study is aimed at evaluating the effect of land use on the environmental chemistry of the metals, the toxicological effects and the potential ecological risk on the populace, hence it was hypothesized that there is a relationship between land use and soil concentrations of heavy metals. Therefore, the objectives of the present study are to determine the effect of land use on the depth distribution of Ni, Cr, Cu, Cd, Zn, Mn and Pb in soils of Abeokuta and Ibadan; to evaluate the contamination/pollution factor and ecological risk associated with the metals and to determine the relationship between some soil chemical characteristics and metal concentrations.

2. Materials and Methods

2.1. Site Description

Abeokuta

Abeokuta is described by Wikipedia (2017) as a city in southwestern Nigeria and capital of Ogun State, with an average temperature of 28 °C and annual rainfall of 1270 mm. The city lies on 7.15° N latitude and 3.35° E longitude, bounded by the eastern bank of Ogun River, 74 km north of Lagos by railway and 130 km by water. Abeokuta is connected to Lagos by rail and serves as the commercial

centre for an area in which cacao, palm kernels, and palm oil are produced. The city is known for its traditional style of hand-woven cotton fabric known as *Adire*, which is dyed with locally produced indigo. A granite outcropping known as Olumo rock is at the city center, and it is the site of traditional local celebrations. The city is home to the Federal University of Agriculture Abeokuta and Ogun State Polytechnic among other institutions.

Ibadan

Ibadan is the capital of Oyo State, with its center at 7.39°N and 3.9°E (Wikipedia, 2017). It is also located in the southwestern part of Nigeria, 128 km northeast of Lagos and 530 km southwest of Abuja. It has an average temperature of 27.5° C and rainfall range of 24.0 to 708.0 (mm/month). Ibadan is a major transit point between the coast and areas to the north. The city is on the railroad line linking Lagos with Kano and is well connected by road to other cities in the region. It is the center of trade for farming areas producing cacao, palm oil, yams, cassava, corn, and fruit. Industries include agricultural processing, brewing, vehicle assembly, and the manufacture of cigarettes. The University of Ibadan and Ibadan Polytechnic are located here. Also Ibadan is the site of several major research institutes, notably the International Institute of Tropical Agriculture, Cocoa Research Institute, Forestry Research Institute, National Horticultural Research Institute, and Nigerian Institute of Social and Economic Research. Most of Nigeria's leading publishing companies are based in the city.

2.2. Sampling and Sample Analyses

The whole sampled areas in Abeokuta and Ibadan have similar geologic formation. The soils are derived from coarse grained granites and gneisses while some parts are of fine grained biotite gneisses and schists. A total number of 96 soil samples were collected from the selected areas. The sampling area at each location is approximately 400 m². The soil samples were collected at two depths (20 cm and 40 cm), in three replications, from 8 different land uses in Abeokuta and Ibadan. The samples were collected using soil auger. The coordinates of each sampling point from a contiguous area (400 m²) were taken with Global Positioning System (GPS). Details of the sampling areas and their characteristics are shown in Table 1. The detailed soil World Reference Based Classes of the soils are also given in the Table.

The collected soil samples were air-dried; stones and tree leaves were removed and then passed through 2 mm sieve. The digestion of the samples were done with ternary mixtures of nitric, sulphuric and perchloric (3:1:1) and concentration of the metals (Ni, Cr, Cu, Cd, Zn, Mn, and Pb) were determined using Atomic Absorption Spectrophotometry, AAS (Donisa *et al.*, 2000). A portion of the sieved soil was also used to determine the following soil properties: soil organic carbon using chromic acid oxidation procedure (Walkley and Black 1939), soil pH using glass electrode pH meter (McLean *et al.*, 1982). The available phosphorus content of the soils was determined by Bray 1 method (Nelson and Sommers, 1996), while total nitrogen was determined using macro-Kjeldahl method (Bremner and Mulvaney, 1982). Electrical conductivity was determined using a conductivity meter while the particle size analysis was done using Bouyoucos

(1962) method. The estimation of the contamination/pollution factor (CPF) of the metals was calculated as $CPF = C/C_0$ [eq. 1] where C is mean concentration of metal in soil and C_0 is background or preindustrial concentrations. The appropriate background value was obtained from values reported for European soils with similar parent materials as indicated above and with pH value between 5 and 6. No such up to date and reliable data/information exists for southwestern Nigerian soils. The values in $mg\ kg^{-1}$ dry soil are 0.5 Cd, 50 Cr, 40 Cu, 30 Ni, 50 Pb, 100 Zn (Gawlik and Bidoglio, 2006); the value used for Mn (476) was the target value reported by the department of petroleum resources, Nigeria (DPR, 2002). The

degree of contamination (DC) of the metals was calculated as the sum of all CPFs: $DC = \sum CPF$ (Fiori *et al.*, 2013) [eq. 2]. Potential risks (*PER*) posed by the presence of the metals was calculated as *PER*: $PER = TRF \times CPF$ [eq. 3], this is calculated separately for each metal, where TRF was the toxic response factor of the element (Hakanson, 1980) as reported by Iwuegbu *et al.* (2015). The TRF values used are: 5, 2, 30, 1, 5, 5, for Pb, Cr, Cd, Zn, Ni and Cu, respectively (Fiori *et al.*, 2013). Potential risks index (*PERI*) was calculated as the sum of all *PER* calculated for each metal: $PERI = \sum PER$. [eq. 4] (Fiori *et al.* (2013); USDOE (2011); USEPA (2001; 2011)).

Table 1. Description of the selected areas used for sampling

Land Use	Latitude (°)	Longitude (°)	Altitude (m)	WRB# Soil Class	Description
Abeokuta^a					
Crop farm	7.20913	3.46024	197	Typic Acrisol	Presence of vegetation including arable crops (yam and cassava). Cropped continuously for 5 years with history of fertilizer application.
Animal farm	7.22683	3.44903	154	Arenic Lixisol	Heap of animal dung, with little or no vegetation
Education	7.09665	3.33038	84	Eutric Leptosol	Presence of vegetation such as weeds. Presence of little stone in the soil
Residential	7.12383	3.34723	110	Typic Acrisol	Presence of vegetation including shade trees and ornamental plant garden
Roadside	6.87846	3.1925	56	Typic Acrisol	Bare land
Industrial	6.89005	3.19866	38	Arenic Lixisol	Bare land, near cement factory
Market	6.84112	3.19208	114	Typic Acrisol	Bare land
Forest	7.21123	3.45953	204	Eutric Nitisol	Secondary forest with little vegetation
Ibadan^b					
Crop farm	7.40309	3.85048	223	Eutric Leptosols	Presence of plantation crops and ornamental plant. Crops grown for more than seven years with fertilizer application and incorporation of crop residues
Animal farm	7.38663	3.83676	192	Eutric Luvisol	Heap of animal dung, with little or no vegetation
Education	7.36710	3.90379	211	Eutric Leptosol	Bare soil with the presence of little stone in the soil
Residential	7.39317	3.79553	218	Typic Acrisol	Presence of little rock and vegetation including weed.
Roadside	7.39985	3.77526	200	Haplic Leptosol	Bare land
Industrial	7.36574	3.85489	184	Haplic Leptosol	Bare land
Market	7.36851	3.66648	241	Typic Acrisol	Bare land
Forest	7.40309	3.85045	218	Typic Acrisol	Secondary forest with little vegetation

^a: WRB, 2006 ; ^b: Soil classification according to Senjobi 2007, Aiboni 2001, respectively.

2.3. Statistical Analysis

Data collected were analysed for their variance using the Statistical Analysis System (SAS) statistical package. The Significant treatment means were separated using Duncan's multiple range test at 5 % probability level. The correlation between the metals and other soil chemical properties were done using same software.

3. Results

3.1. Soil Chemical Properties and Heavy Metal Concentration Effect of Soil Depth

The effect of soil depth on soil chemical properties and heavy metal content (mean across land use) is shown in Table 2. It was observed that soil depth had no effect on pH, electrical conductivity (EC) and clay content at Abeokuta while the pH and clay at 20-40 cm were significantly ($p < 0.05$) higher than those of 0-20 cm at Ibadan. At both locations, 0-20 cm soil depth had significantly higher soil total nitrogen and organic carbon. Analytical values of soil P, Ni, Cr, Cd, Zn and Mn at both soil depths were similar in Abeokuta and Ibadan but the concentrations of Cu and Pb were significantly higher in 0-20 cm at both locations (Table 2).

Table 2. Effect of soil depth on soil properties and the heavy metals concentration

Depth (cm)	Soil pH	EC	Clay	N	Org C	P	Ni	Cr	Cu	Cd	Zn	Mn	Pb
		$\mu\text{S cm}^{-1}$	----- (%) -----			-----mg kg ⁻¹ -----							
Abeokuta													
0-20	5.69a	0.12a	7.91a	0.08a	^a 0.98	16.33a	2.88a	15.25a	16.03a	5.28a	48.43a	288.00a	16.03a
20-40	5.72a	0.08a	8.38a	0.04b	^b 0.46	10.57a	2.79a	15.77a	8.95 ^b	2.08a	33.66a	279.00a	8.95b
Ibadan													
0-20	5.56 ^b	0.28a	5.17 ^b	0.08a	^a 1.03	24.19a	6.99a	16.49a	21.72a	6.35a	223.60a	557.00a	21.72a
20-40	5.74 ^a	0.57a	6.28 ^a	0.02b	^b 0.37	22.75a	6.35a	16.48a	14.83b	6.99a	238.70a	596.60a	14.83b

Alphabets a,b, are Duncan alphabets. Means with the same alphabet(s) in a column under same location are not significantly different from each other at $p < 0.05$

Effect of Land Use

Table 3 shows the effect of land use types on the soil heavy metals and other soil properties. At Ibadan, the soil EC, clay, N, organic C were not statistically different ($p > 0.05$) across land use types. However, at Abeokuta, crop farm had statistically similar soil pH with those of the industrial, animal farm, and forest land uses but significantly higher than those of other land uses. The lowest soil pH was recorded at the market land use. Similarly, at Ibadan, industrial land use had significantly higher soil pH compared with those of animal farm, educational and market land uses. Crop farm and market land use had significantly higher soil clay than other land use. At both locations, the soil P was significantly higher at the animal farm while the least soil P was observed at Ibadan

residential area and crop farm at Abeokuta. The concentrations of Ni, Cr, and Cu at both locations; Zn at Abeokuta, Cd and Pb at Ibadan were similar among the different land uses. Educational site at Abeokuta, however, had significantly ($p < 0.05$) higher soil Cd with the least value in animal farm while industrial land use had the highest amount of soil Zn at Ibadan. The value is significantly ($p < 0.05$) higher than educational and residential land uses that recorded the least values. Manganese is more concentrated in the industrial area at Ibadan with the lowest concentration at the market sites. Conversely, market, animal farm and forestland uses had the highest Mn at Abeokuta. The concentration of Pb at the education land use was significantly higher than the values in the other land uses.

Table 3. Some soil chemical properties and heavy metals concentration (values across soil depths)

Depth (cm)	Soil pH	EC	Clay	N	Org C	P	Ni	Cr	Cu	Cd	Zn	Mn	Pb
		$\mu\text{S cm}^{-1}$	----- (%) -----			-----mg kg ⁻¹ -----							
Abeokuta													
Crop farm	6.06 ^a	0.05c	6.57a	0.07 ^{ab}	0.67a	5.23 ^b	3.04a	15.08a	3.28a	3.02 ^{ab}	13.91a	318.40ab	5.72b
Industrial	5.81 ^{ab}	0.07bc	9.58b	0.06 ^{ab}	0.70a	11.48 ^b	2.33a	15.59a	3.81a	3.80 ^{ab}	20.13a	349.20b	7.58ab
Animal farm	5.75 ^{abc}	0.25a	5.80b	0.092 ^a	0.99a	43.62 ^a	3.12a	14.64a	4.20a	1.69 ^b	84.75a	373.10a	9.73ab
Forest	5.74 ^{abc}	0.08bc	6.33b	0.08 ^{ab}	0.73a	9.05 ^b	3.16a	17.79a	3.81a	2.72 ^b	18.43a	452.00a	11.41ab
Road side	5.68 ^{bc}	0.04c	6.67b	0.05 ^{ab}	0.64a	9.18 ^b	3.22a	13.98a	4.40a	1.78 ^b	66.65a	283.30ab	12.01ab
Education	5.66 ^{bc}	0.07bc	6.00b	0.07 ^{ab}	0.76a	8.47 ^b	2.40a	13.82a	3.91a	11.50 ^a	55.38a	359.50a	14.17a
Residential	5.56 ^{bc}	0.09bc	9.33b	0.05 ^{ab}	0.53a	10.55 ^b	2.89a	14.58a	2.80a	3.06 ^{ab}	24.13a	240.40ab	9.65ab
Market	5.41 ^c	0.15ab	14.90a	0.04 ^b	0.72a	9.99 ^b	2.53a	18.60a	5.16a	1.86 ^b	44.99a	467.00a	9.68ab
Ibadan													
Crop farm	5.79 ^{ab}	0.11a	4.93a	0.05a	0.63a	12.49 ^c	4.74a	16.33a	7.65a	3.59a	55.9 ^b	587.70ab	15.65a
Industrial	5.98 ^a	0.29a	5.83a	0.06a	0.65a	14.56 ^c	13.81a	17.52a	12.71a	3.68a	664.0 ^a	834.00a	15.93a
Animal farm	5.42 ^{cd}	0.62a	5.47a	0.08a	1.00a	66.31 ^a	5.49a	16.81a	18.45a	1.13a	117.5 ^b	494.40b	14.60a
Forest	5.73 ^{abc}	1.70a	6.53a	0.04a	0.40a	24.19 ^{bc}	4.43a	19.38a	11.63a	3.90a	385.6 ^{ab}	649.30ab	15.28a
Road side	5.76 ^{ab}	0.15a	5.60a	0.05a	0.74a	9.31 ^c	4.90a	14.89a	16.80a	5.23a	119.9 ^b	508.80b	18.34a
Education	5.63 ^{bc}	0.22a	6.03a	0.04a	0.68a	15.20 ^c	4.41a	14.87a	9.28a	0.80a	86.9 ^b	472.80b	14.48a
Residential	5.69 ^{abc}	0.14a	5.13a	0.05a	0.57a	8.65 ^c	5.10a	16.29a	9.43a	1.17a	89.2 ^b	654.50ab	17.34a
Market	5.22 ^d	0.18a	6.23a	0.07a	0.92a	37.05 ^b	10.49a	15.80a	9.13a	3.49a	330.1 ^{ab}	421.70b	15.68a

Alphabets a,b,c, are Duncan alphabets. Means with the same alphabet(s) in a column under same location are not significantly different from each other at $p < 0.05$

Effect of Soil Depth, Location and Land Use

The effect of soil depth, location and land use on the soil properties and heavy metal content for the combined data is shown in Table 4. It was observed that soil depth has no significant effect on the soil properties and heavy metals studied except soil organic carbon. The soil organic C was concentrated at the 0-20 cm depth; the value is twice that of 20-40 cm depth. On comparing both locations, the results shows that soil pH, EC, total nitrogen, organic carbon, soil Cd and Pb were similar between the locations. Soil clay and Mn concentration was however, significantly higher at Abeokuta. On the other hand, the amount of soil P, Ni, Cu and Zn were significantly higher at Ibadan. Soil pH was significantly higher in crop farm, industrial, forest and roadside. The values noted in the crop farm and industrial land use was significantly higher than the pH values observed in educational and residential land use. The land use types

have no effect on the soil EC, N, organic C, Ni, Cr, Cd and Mn, but clay at the market is significantly higher than the values from other land uses. There was significantly higher concentration of phosphorus in the animal farm. The value observed was more than double that observed in market land use. The lowest P concentrations were observed at residential, educational, crop farm and roadside. The likely reasons for the high P in animal farm have been given earlier in the text. The concentration of Cu was significantly higher in animal farm, though not statistically different from the values from other land uses. The lowest value was observed at the crop farm. Soil Zn concentration was highest in the industrial land; the value was however, similar to the Zn concentration at animal farm, forest and roadside and market land. The lowest soil Zn was recorded in crop farm, educational and residential land uses, the values were significantly lower than that of the industrial land use.

Table 4. Effect of soil depth, location and land use (means of the locations) on some soil chemical properties and heavy metal concentration

	Soil pH	EC	Clay	N	Org. C	P	Ni	Cr	Cu	Cd	Zn	Mn	Pb
		μScm^{-1}	----- (%) -----			----- mg kg^{-1} -----							
Soil Depth(cm)													
0-20	5.63a	0.19a	7.33a	0.08a	0.98a	20.26a	4.62a	15.25a	8.99a	3.64a	135.99a	457.80a	16.37a
20-40	5.73a	0.33a	6.54a	0.06a	0.46b	16.66a	4.89a	15.77a	6.81a	2.92a	136.18a	436.80a	11.89a
Locations													
Abeokuta	5.71a	0.09a	8.15a	0.06a	0.74a	13.45b	2.84b	14.53a	3.92b	3.68a	41.04b	567.80a	10.00a
Ibadan	5.65a	0.46a	5.72b	0.05a	0.70a	23.47a	6.67a	16.48a	11.88a	2.88a	231.13a	317.9b	13.27a
Land Use													
Crop farm	5.93a	0.08a	5.75b	0.05a	0.67a	8.88c	3.89a	15.08a	5.46b	3.30a	34.90b	433.80a	10.68b
Industrial	5.89a	0.18a	7.71b	0.06a	0.70a	13.02bc	8.07a	15.59a	8.26ab	3.74a	342.10a	441.60a	11.75ab
Animal farm	5.58b	0.43a	5.63b	0.08a	0.99a	54.97a	4.30a	14.64a	11.33a	1.41a	101.1ab	433.80a	12.16ab
Forest	5.73ab	0.89a	6.43b	0.06a	0.73a	16.67bc	3.79a	17.79a	7.72ab	3.31a	202.00ab	550.70a	13.34ab
Road side	5.72ab	0.09a	6.13b	0.05a	0.64a	9.25c	4.06a	13.98a	10.60ab	3.51a	93.30ab	396.10a	21.61a
Education	5.65b	0.14a	6.02b	0.05a	0.76a	11.84c	3.41a	13.82a	6.59ab	6.15a	71.10b	416.10a	14.32ab
Residential	5.63b	0.11a	7.23b	0.05a	0.53a	9.59c	3.99a	14.58a	6.11ab	2.15a	56.60b	443.00a	17.99ab
Market	5.31c	0.17a	10.57a	0.05a	0.72a	23.52b	6.51a	18.60a	7.14ab	2.68a	187.50ab	444.40a	11.18b

Alphabets a,b,c,are Duncan alphabets. Means with the same alphabet(s) in a column under same depth, location and land use are not significantly different from each other at $p < 0.05$

Relationship between Soil Chemical Properties and Metal Concentrations

The correlation between the soil chemical properties and heavy metal content is shown in Table 5. The soil pH was negatively correlated with the soil phosphorus while the soil EC was positively correlated with Cr, Cu and Zn ($p < 0.05$). Soil nitrogen was also shown to be positively correlated with organic C, P, Cu, Zn and Pb. Similar significant and positive

correlation were observed between organic C and P, Ni, Cu, Zn and Pb. Soil P and Cu was also positive and significant ($p < 0.01$). Nickel was positive and significantly correlated with soil Cr, Cu, Zn and Mn while soil Zn and Mn correlated with Cr. There was also a positive and significant correlation between soil Cu and soil Zn, Mn and Pb. The correlation between soil Zn and Mn was significant and positive. The correlation coefficient between soil Mn and Pb

Table 5. Correlation between soil chemical properties and metal concentrations (mean of the locations) n=96

Depth (cm)	pH	EC	Clay	N	Org C	P	Ni	Cr	Cu	Cd	Zn	Mn
EC	0.01											
Clay	-0.04	-0.07										
N	-0.12	0.04	-0.14									
Org C	-0.13	-0.01	-0.14	0.93**								
P	-0.33**	0.05	-0.11	0.20*	0.21*							
Ni	-0.03	0.01	-0.12	0.21*	0.33**	0.14						
Cr	-0.17	0.24*	-0.01	-0.02	0.03	0.04	0.41**					
Cu	-0.20	0.07*	0.25*	0.33**	0.44**	0.30**	0.33**	0.20				
Cd	-0.10	0.08	-0.04	0.10	0.12	-0.08	0.10	0.03	-0.06			
Zn	0.02	0.42**	-0.11	0.22*	0.28**	0.06	0.81**	0.43**	0.36**	0.16		
Mn	-0.10	0.20	-0.30**	0.11	0.18	0.05	0.45**	0.47**	0.33**	0.19	0.46**	
Pb	-0.18	0.01	-0.02*	0.26*	0.32**	0.02	0.20	0.11	0.68**	0.13	0.18	0.39**

*, ** significant at $P \leq 0.05$ and ≤ 0.01 , respectively; EC = Electrical conductivity; Org C = organic carbon

Soil Contamination and Ecological Risk Indices

The estimation of the contamination/pollution factor (CPF) and the degree of contamination of the metals are shown in Table 6. It was observed that Cd and Zn had the highest CPF across soil depth, locations and land use. The least CPF values were observed in Ni. The general sequence of CPF values are as follows: Cd > Zn > Mn > Cr > Pb > Cu > Ni. However,

the degree of contamination values indicated that the top soil was more contaminated with metals while Ibadan soils were also marginally more polluted compared with Abeokuta soils. Among the land uses, educational, industrial and forestland uses have higher degree of contamination than other land use while the least value was observed in the animal farm.

Table 6. Contamination/pollution factor and degree of contamination of the soil heavy metals as affected by soil depth, location and land use types

	Contamination/pollution factor							Degree of Contamination
	Ni	Cr	Cu	Cd	Zn	Mn	Pb	
<i>Soil Depth(cm)</i>								
0-20	0.15	0.31	0.22	7.28	1.36	0.96	0.33	10.61
20-40	0.16	0.32	0.17	5.84	1.36	0.92	0.24	9.01
Mean	0.16	0.31	0.20	6.56	1.36	0.94	0.28	9.81
<i>Locations</i>								
Abeokuta	0.09	0.29	0.10	7.36	0.41	1.19	0.20	9.65
Ibadan	0.22	0.33	0.30	5.76	2.31	0.67	0.27	9.85
Mean	0.16	0.31	0.20	6.56	1.36	0.93	0.23	9.75
<i>Land Use</i>								
Crop farm	0.13	0.30	0.14	6.60	0.35	0.91	0.21	8.64
Industrial	0.27	0.31	0.21	7.48	3.42	0.93	0.24	12.85
Animal farm	0.14	0.29	0.28	2.82	1.01	0.91	0.24	5.70
Forest	0.13	0.36	0.19	6.62	2.02	1.16	0.27	10.74
Road side	0.14	0.28	0.27	7.02	0.93	0.83	0.43	9.90
Education	0.11	0.28	0.16	12.30	0.71	0.87	0.29	14.73
Residential	0.13	0.29	0.15	4.30	0.57	0.93	0.36	6.73
Market	0.22	0.37	0.18	5.36	1.88	0.93	0.22	9.16
Mean	0.16	0.31	0.20	6.56	1.36	0.93	0.28	9.81

The potential risks and the risk index posed by the presence of the metals are shown in Table 7. It was evident that Cd is a serious ecological risk in the study area irrespective of soil depth and location. The risk however, is higher at 0-20 cm depth and also at Abeokuta. The Zn and Pb in the soil also has

higher ecological risk that Cu, Cr and Ni but lower than Cd. Similar pattern of risk was observed across land use, however educational, industrial and road side land uses had higher risk index than other land use types. The least risk index is obtained in the animal farm.

Table 7. Potential ecological risk and ecological risk index of the soil heavy metals as affected by soil depth, location and land use types

	Potential Ecological risk						Potential Ecological Risk Index
	Ni	Cr	Cu	Cd	Zn	Pb	
<i>Soil Depth(cm)</i>							
0-20	0.77	0.61	1.12	218.40	1.36	1.64	223.90
20-40	0.82	0.63	0.85	175.20	1.36	1.19	180.05
Mean	0.79	0.62	0.99	196.80	1.36	1.41	201.97
<i>Locations</i>							
Abeokuta	0.47	0.58	0.49	220.80	0.41	1.00	223.75
Ibadan	1.11	0.66	1.49	172.80	2.31	1.33	179.69
Mean	0.79	0.62	0.99	196.80	1.36	1.16	201.72
<i>Land Use</i>							
Crop farm	0.65	0.60	0.68	198.00	0.35	1.07	201.35
Industrial	1.35	0.62	1.03	224.40	3.42	1.18	232.00
Animal farm	0.72	0.59	1.42	84.60	1.01	1.22	89.55
Forest	0.63	0.71	0.97	198.60	2.02	1.33	204.26
Road side	0.68	0.56	1.33	210.60	0.93	2.16	216.25
Education	0.57	0.55	0.82	369.00	0.71	1.43	373.09
Residential	0.67	0.58	0.76	129.00	0.57	1.80	133.38
Market	1.09	0.74	0.89	160.80	1.88	1.12	166.51
Mean	0.79	0.62	0.99	196.88	1.36	1.41	202.05

4. Discussion

4.1. Effect of Land Use

High soil organic matter is known to correlate with high biological activities. The top 20 cm (plough layer) is known to be concentrated with microorganisms that are involved in the mineralization of applied organic materials, therefore the high soil N and organic C. Data on soil depth indicated that there is a movement of the metals in the soil; hence the similarities in values across depth except Cu and Pb that were concentrated in the top soil relative to the subsoil. Similar results have been reported by Azeez *et al.* (2011). It, thus, implies that the inhalation of these metal polluted dusts from these sites could prove dangerous since metals, like Pb is concentrated at the uppermost soil layer.

The higher pH of the crop farm at Abeokuta and other land use implies that the heavy metals and other micronutrients may be comparatively deficient or unavailable in the soil of the land uses compared with others; however the low pH of the market land use suggests the likelihood of having higher metal content. Low soil pH has been reported to cause low soil adsorption and high concentration of heavy metals in soil solution (Salt *et al.*, 1995). The soil pH was acidic and expected to promote the build-up of the metals in soil solution (Salt *et al.*, 1995). At Abeokuta, significantly higher EC and soil N was observed in animal farm while the corresponding lowest values were observed at the roadside and market land use. The deposition of animal manures on the farm could have

increased the soil dissolved salt and enriched the soil with N. Typical of animal farm on free-range, the farm animals are known to scavenge for food and in the process excrete urine and faeces indiscriminately on the soil. Similar, high EC values have been reported by Azeez *et al.* (2011) in market dumpsite where animals have been known to graze. The reason for high soil P at animal farm is most probably because of free-range adopted on the animal farms in the study areas. Here animal scavenge for food, and in the process litter the soil with their litter and urine. The implication of the high Cd and Pb at educational sites and Zn and Mn at the industrial land uses is that soils of these land uses are potential risk. The industries might have polluted the soil through their waste discharge by the air and wastewaters while the soils of the educational areas are potential contaminants if ingested or inhaled (Moller *et al.*, 2005). The high soil P (above the critical soil P of 15 mg kg⁻¹ for southwest Nigerian agricultural soils), Ni, Cu and Zn at Ibadan implies that Ibadan is more polluted with metals compared with Abeokuta. This is because of its higher population and the residents of Ibadan are known to engage in several commercial and industrial activities more than Abeokuta. Ibadan (with 11 local governments) has a population estimate of 3.6 million while Abeokuta (comprising of Abeokuta north and south, Odeda, Ifo and Ewekoro local government) has a population of about 1.2 million inhabitants in 2006 national population census. The concentration of industries is more in Ibadan and the city is the largest city in West Africa. On the other hand, Abeokuta is

popularly referred to as a 'civil service' city because majority of the inhabitant are government workers or workers of the private sectors. The number of industries in Abeokuta town is low. Due to the positive relationship between low soil pH and metals build-up (Salt *et al.*, 1995), it then means soil of the market land use probably will be more contaminated. This is evident in the present study, most of the significantly higher metal concentration levels are observed in the market dumpsite.



Figure 1. Map of Abeokuta. Source <https://www.google.com.ng>

4.2. Effect of Soil Depth, Location and Land Use

The high zinc content of the industrial soils could be related to the continuous input of the metal from the industries through vehicle and heavy machines exhaust emissions (Ward, 1989). Concentration of soil Pb was significantly higher at the roadside and lowest in the crop farm. The high Pb on the roadside could be due to the atmospheric deposition of Pb from the exhaust of vehicles using the roads. There are evidences of Pb from gasoline and Cu, Zn, and Cd from car parts (Wilcke *et al.*, 1998). The values of soil Pb in industrial, animal farm, forest, educational and residential were statistically similar. Atmospheric deposition (due to industrialization and human activities) of the metal pools has also been given as the reason for the accumulation of the metals in the soil close to industries (Niu *et al.*, 2013; Luo *et al.*, 2009). A similar result was reported in Sweden, where increasing industrial activity was reported to increase soil Pb and Cd concentration by 50 % (EEA, 1998) and in Nigeria by Iwegbue *et al.* (2012). The rather high amount of Cd in the crop farms could have been due to the application of phosphatic fertilizers on the farm. The two farms studied have histories of phosphorus fertilizer application. Most phosphate fertilizers have been reported to contain Zn, As, Cd and Cr from the phosphate rock used as the raw material for the P fertilizer manufacture (Iwegbue *et al.*, 2012; Yang *et al.*, 2004; Luo *et al.*, 2007). Generally, the mean concentration of the metals in both locations shows the values were lower than those reported for some cities in developed countries. The values were lower than those of Naples, Italy (Imperato *et al.*, 2003); Palermo, Italy (Manta *et al.*, 2002); Bangkok, Thailand (Wilcke *et al.*, 1998); Seville, Spain (Madrid *et al.*, 2002); Madrid, Spain (Miguel *et al.*, 1998); Seoul, Korea (Chon *et al.*, 1995); Turku, Finland (Salonen and Korkka-Niemi, 2007); Damascus, Syria (Moller *et al.*, 2005); Hong Kong, China (Li *et al.*, 2004); Shenyang, China (Sun *et al.*, 2010); Shanghai, China (Shi *et al.*, 2008); Beijing, China (Xia *et al.*, 2011). The values are however higher than that previously reported for some southwestern Nigerian soils (Azeez *et al.*, 2011, 2014), including some of the sites sampled for the present study, but lower than that

reported for Ijebu-North in Ogun state, Nigeria (Adedeji *et al.*, 2013). Similar results have also been reported for some dumpsite soils by Iwegbue *et al.* (2010). This implies the gradual build-up of the metals in the cities with time. Soil Zn in Ibadan at industrial sites is higher than the averages of the other cities. This connotes Zn pollution of the soil.

4.3. Relationship between Soil Chemical Properties and Metal Concentrations

Positive and significant correlation observed between organic matter (measured as organic carbon) implies the soil heavy metals are mostly organic bound. Studies have also reported correlation between Pb and organic matter (Kabała and Szerszen, 2002), due to the complexation of Pb by humic substances (Donisa *et al.*, 2000; Azeez *et al.*, 2011). Gonzalez *et al.* (2006) and Du Laing *et al.* (2009) opined that organic carbon is a major sink for heavy metals. Correlation of soil nitrogen and the metals is also expected because, soil N is closely related to organic matter in most tropical soils.



Figure 2. Map of Ibadan. Source <https://www.google.com.ng>

4.4. Soil Contamination and Ecological Risk Indices

Data obtained from the estimation of the contamination/pollution factor, degree of contamination, potential ecological risk and the ecological risk indices revealed that the soils were highly contaminated with Cd. The contamination of the soil by Zn was moderate while the levels of contamination of the other studied metals were low in the soil. However, the degree of contamination of the soils were generally very high irrespective of the soil depths, location and the land use types except the considerable degree of contamination observed in the animal farm. The metals generally have low potential ecological risk except Cd, which poses a high ecological risk. The ecological risk index revealed that the soil has moderate index (Fiori *et al.*, 2013); similar results was reported by Iwegbue (2014) and Iwegbue *et al.* (2012) for the Niger Delta region of Nigeria.

Conclusions

Depth distribution of metals in Abeokuta and Ibadan soils were similar but soils from Ibadan were more contaminated. Nickel, Cu and Zn accumulated in Ibadan soils while soils from Abeokuta had higher concentration of Mn. Animal farm had higher amount of Cu but concentration of Zn was higher in industrial, animal farm, forest, roadside, and market. The values were higher than those of crop farm, educational and residential land use. Soil from roadside had the highest amount of lead. The soil metals appeared bound to organic matter. Source identification indicated that the contamination of the soil was mainly from industrial and anthropogenic sources. There is a gradual build-up of metals in the selected

land uses. The soil is highly contaminated with Cd moderately contaminated with Zn while the levels of contamination of the other studied metals are low. The metals generally have low potential ecological risk except Cd which poses a high ecological risk. The ecological risk index revealed that the soil has moderate index. The soil metal concentrations are lower than the amount in other developed cities around the world.

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