

Original Research Article

Assessment of the Levels of Heavy Metal Contamination in Soils Around Selected Municipal Solid Waste Dumpsites in Benin City, Nigeria using Pollution Indices

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ARTICLE INFORMATION

Article history:

Received 28 August, 2018

Revised 04 October, 2018

Accepted 05 October, 2018

Available online 30 December, 2018

Keywords:

Municipal solid waste dumpsite

Heavy metals

Pollution indices

Benin City

Contamination

ABSTRACT

Contamination levels assessment of heavy metals such as Cu, Pb, Mn, Ni, Zn, Cd and Cr in soils around municipal solid waste dumpsites in Benin City, Edo State, Nigeria was carried out. The aforementioned metals were analytically determined with an atomic absorption spectrophotometer. The mean concentration levels of heavy metals in the studied dumpsites ranged from 7.63 ± 0.06 to 37.27 ± 0.06 mg/kg for Cu, 1.23 ± 0.21 to 8.30 ± 0.01 mg/kg for Pb, 1.30 ± 0.26 to 9.27 ± 0.31 mg/kg for Mn, 1.00 ± 0.00 to 5.13 ± 0.06 mg/kg for Ni, 5.00 ± 0.17 to 37.93 ± 0.87 mg/kg for Zn, 1.00 ± 0.00 to 6.79 ± 0.02 mg/kg for Cd, and 0.91 ± 0.01 to 5.60 ± 0.36 mg/kg for Cr. Zn was found to be more abundant and was closely followed by Cu while Cr was least abundant in the studied sites. The contamination and pollution index (C/PI) of the analysed heavy metals showed that only Cd was in the pollution ranges with high risk degree while other analysed heavy metals were in the contamination ranges with low risk degree as indicated by the C/PI and the potential ecological risk index (PE_R^I) respectively. The pollution load index (PLI) ranges and mean levels were in the following order: Dumpsite II (1.41 – 6.1) averaging 3.41 > dumpsite I (1.85 – 3.82) averaging 2.76 > dumpsite III (1.08 – 2.92) with an average of 1.95, which represents the number of times the metal content in the soil exceeds the average natural background concentration.

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1. INTRODUCTION

Toxic heavy metals from waste dumpsites may contaminate soils, plants, water supplies and human food chain (Lokeshappa et al., 2012). The inability to manage these wastes effectively in most developing and some developed countries becomes an issue of great concern because apart from the destruction of aesthetic of landscape by the waste dumpsites, some of the municipal solid wastes contain both organic and in-organic toxic pollutants like heavy metals which threaten human health and the entire ecosystem (Anake et al., 2009).

Heavy metals refer to any metallic chemical element in the periodic table having relatively high density (density greater than 5g/cm^3) and are toxic at low concentration. The condition of heavy metals in soils is problematic due to their persistence and non-biodegradability in the environment (Yuan *et al.*, 2004; Hong *et al.*, 2014). In recent years, there has been growing concerns over increased contamination of soils and sediments from various anthropogenic sources like illegal dumping of wastes on land and water.

Heavy metals also occur naturally in soils either from the processes of weathering of parent materials or due to the geochemical component or formation of the soil area but usually in trace amount (Narwal *et al.*, 1999). The accumulation of metals in soils from both natural and anthropogenic sources occur in the same way, thus making it difficult to identify and determine the origin of heavy metals present in the soil (Caplat *et al.*, 2005; Idris *et al.*, 2007). The largest fraction of heavy metals in soils is associated with the solid phase of that soil. The problem of pollution arises when heavy metals are mobilised into soil solution and then taken up by plants or transported to surface or ground water (Kabala and Singh, 2001). The solubility of compounds or ions of metals in soils is controlled by reactions in solid Phases. These reactions include mineral precipitation and dissolution, ion exchange, redox reaction, adsorption and desorption reactions, aqueous complexation, biological immobilization and mobilization and plant uptake through diffusion (Shiowatana *et al.*, 2001). However, not all the reaction processes in soil chemical and biological processes are equally important for each metal element, but all metals are affected by soil pH and biological processes (Shiowatana *et al.*, 2001; Kabala and Singh 2001). A study of the levels of contamination and pollution of heavy metals in soils around municipal solid waste dumpsites is particularly important, especially in developing country like Nigeria due to the unprofessional and lawless manner with which wastes are disposed and also for the assessment of the possible influence of anthropogenic activities on lands and ground water.

In this study, the levels of soil heavy metals contamination and pollution was assessed based on contamination and pollution index (C/PI), pollution load index (P/LI) from contamination factors (CF), geo-accumulation index (I_{geo}) and the potential ecological risk index (PE_R^i). The standards employed for interpreting soil heavy metal contamination / pollution (C/P) varies from country to country based on chosen factors (Lacutus, 2002). In Nigeria, the pollution index represents the metal content effectively measured in the soil by chemical analysis and the reference value of contamination obtained using a standard table formulated by the Department of Petroleum Resources of Nigeria, DPR (DPR, 2002) for maximum allowable concentration of heavy metals in soils.

2. MATERIALS AND METHODS

2.1. Study Area

The study area is within Benin City metropolis, the capital of Edo state, Nigeria and is located in the south-south geopolitical zone of Nigeria; bounded by latitudes $6^{\circ}15'N$ to $6^{\circ}30'N$ and longitudes $5^{\circ}30'E$ to $5^{\circ}45'E$ and area of about 500 square kilometres. The climatic condition falls within the Rain forest type and similar to other parts of southern Nigeria. Limonitic coatings are responsible for the brown reddish-yellowish colour. The formation is covered with loose brownish sand varying in thickness and is about 800m thick; almost all of which is water bearing with water level varying from about 20 to 52 m. It is generally believed to be highly permeable, porous and prolific in water yield (Short and Stauble, 1967; Kogbe, 1989; Adaikpoh *et al.*, 2005; Adaikpoh and Kaizer, 2012). The map of Benin showing soil sample collection points and a table showing sampling sites description with their geographical position coordinates are presented in Figure 1 and Table 1 respectively.

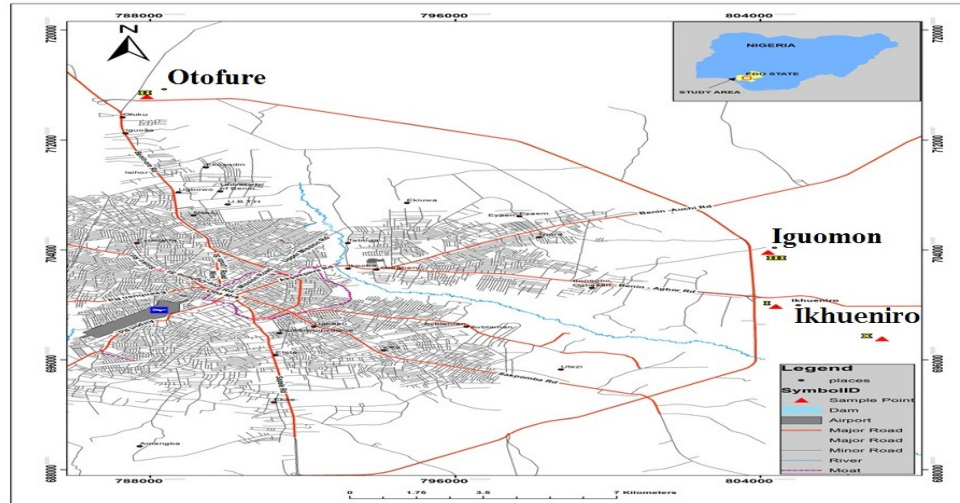


Figure 1: Map of Benin showing samples location

Table 1: Sampled sites description and coordinates

Sampled sites	Location of Dumpsite	Type of waste	Age of dumpsite	Size of dumpsite	Coordinates (Latitude & Longitude)
Dumpsite (I)	Ikhueniro dumpsite; Ikhueniro community, Benin Agbor road (Bye pass) Benin City	Domestic	15yrs	52,000 m ²	6°19'28.261" N5°45'04.158"E
Dumpsite (II)	Otofure dumpsite; Otofure community, Oluku Bye pass, Benin City	Domestic	Above 17yrs	37,500 m ²	6°27'47.599" N5°36'10.397"E
Dumpsite (III)	Iguomon dumpsite; Iguomon community, Benin Lagos express way (Bye pass), Benin City	Domestic	15yrs	58,560 m ²	6°21'36.360" N5°44'58.085"E
Control site (X)	Farm land at Ikhueniro community, Benin Agbor road, Benin City	-	-	-	6°18'11.394" N5°46'34.226"E

2.2. Sample Collection and Preparation

Composite soil samples were collected around three (3) Government approved municipal solid waste dumpsites in Benin City, using a stainless-steel spade at depths of 0 – 15, 15 – 30 and 30- 45 cm, representing top soils, sub soils and bottom soils respectively. Three soil samples per points from the three depths were bulked together to form one composite sample. At each studied dumpsite, six (6) different points were randomly chosen (50 metres away from the centre of each studied dumpsite) for sampling. The composite soil samples from the six different points in each studied dumpsite were labelled A, B, C, D, E and F for dumpsite (I); G, H, I, J, K and L for dumpsite (II); and M, N, O, P, Q and R for dumpsite (III), to give a total of eighteen (18) composite soil samples from the three studied dumpsites. The gradient (high and low gradient) and the direction of flow of erosion were also considered for each sampling point (spot). Control soil samples were also obtained in similar manner from a farm land in the adjoining area of the solid wastes

dumpsite (500 metres away from the studied wastes dumpsites) to serve as control and was labelled sample 'X'. The control site was unaffected by dumping of waste materials. The geographical position coordinates of the sampled sites were identified and mapped using global position system (GPS). Soil samples collected were transferred into a black polythene bag, labelled properly and transported to the laboratory for analysis. Soil samples were air-dried for a period of two weeks in a well-ventilated space. Samples were homogenized by grinding in porcelain mortar and sieved through a 2mm (10 meshes) stainless sieve. The air-dried < 2mm soil samples were oven-dried at $105 \pm 0.5^\circ\text{C}$ to a constant mass, cooled and stored in a labelled airtight plastic Cans prior to analysis (Allen *et al.*, 1974; Okuo *et al.*, 2016a).

2.3. Determination of Total Heavy Metals in the Soil

Total heavy metals determination was carried out in accordance with the USEPA method described by Khodadoust *et al.* (2004) and Ilori *et al.* (2012). Five (5) mL of aqua regia solution and 1 mL of perchloric acid were added to two grams of soil sample in a 150 mL digestion tube and digested on a heating digester until white fumes of perchloric acid appeared. All glassware used were soaked and washed with chromic acid and rinsed with distilled water. Bulk scientific standard solution was used to calibrate the Atomic Absorption Spectrometer (Bulk Scientific VGP 210). Procedural blank samples were subjected to similar extraction method using the same amount of reagents.

2.4. Pollution Indices

2.4.1. Contamination/pollution index (C/PI)

This was calculated using Equation (1).

$$C/PI = \frac{\text{Concentration of metals in soil}}{\text{Target value from reference table}} \quad (1)$$

A distinction between soil contamination and pollution range will be establish by means of the contamination/pollution index (Lacutus, 2002).

2.4.2. The Geo-accumulation index (I_{geo})

The I_{geo} values were calculated using the Muller's expression in Equation (2) (Sucharova *et al.*, 2003; Selvaraj *et al.*, 2004; Reddy *et al.*, 2004).

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5B_n} \right) \quad (2)$$

2.4.3. Pollution load index (PLI)

The PLI was obtained as a contamination factor (CF) of each metal with respect to the natural background value in the soil (Tomllinson *et al.*, 1980; Angulo, 1996; Usero *et al.*, 2000) by using Equations (3) and (4).

$$CF = \frac{C_{sample}}{C_{Background}} \quad (3)$$

$$PLI = [CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n]^{1/n} \quad (4)$$

2.4.4. Potential ecological risk index (PERI)

PERI is formed by three basic modules: degree of contamination (C_D), toxic-response factor (T_R) and potential ecological risk factor (E_R). According to this method, the potential ecological risk index of a single element (E_R^i) and comprehensive potential ecological risk index (RI) can be calculated with equations 5 -7:

$$C_f^i = \frac{C_D^i}{C_R^i} \quad (5)$$

$$E_R^i = T_R^i \times C_f^i \quad (6)$$

$$RI = \sum_{i=1}^m E_R^i \quad (7)$$

The biological toxic-response factor (T_R^i) of a single metal element is; Zn = Mn = 1, Cr = 2, Cu = Pb = Ni = 5 and Cd = 30 (Hakanson, 1980; Singh *et al.*, 2010; Jiang *et al.*, 2014)

2.5. Statistical Analysis of Data

The mean concentration levels of heavy metals were statistically analysed using Genstat 8.1 Edition. A *t*-test was used to verify whether there were statistically significant differences in the concentration levels of the analysed heavy metals amongst the studied sites (the control and studied dumpsites). From the ANOVA, soil heavy metals variability was estimated using mean and coefficient of variation (CV %). Heavy metals with larger CV values are more variable than those with smaller CV values. Ranking of variability was done using the Wilding's (1985) classification scheme described by Ezeaku *et al.* (2015). Little variation (CV ≤ 0 - 15%), moderate variation (CV = 16 - 35%), high variation (CV ≥ 36%). Simple correlation analysis was executed to reveal the magnitudes and directions of relationships between analysed soil heavy metals.

3. RESULTS AND DISCUSSION

From the result of heavy metal levels in the studied dumpsites (Tables 2-4), the concentration levels of the analysed heavy metals were low with the exception of Cd when compared with the permissible limits set by local and international guidelines organizations.

3.1. Copper (Cu)

The overall mean levels of Cu distribution in soil samples in the studied dumpsites varied from 7.63 ± 0.06 to 37.27 ± 0.06 mg/kg against the mean level of 5.23 ± 0.32 mg/kg in control site (Tables 2-4). Copper was ranked second behind Zn as the most abundant metal in the studied sites. The maximum range of Cu in the studied dumpsites was slightly above the Target value (36 mg/kg) of DPR (2002) for heavy metal contamination / pollution levels or limits. With respect to contamination /pollution index, the soils from the studied dumpsites can be ranked as slightly contaminated to very severe contamination with Cu (Table 5). However, the amount of copper due to contamination factor (CF) varied from 1.46 - 7.13 in the studied dumpsites (Table 6). From the index of geo-accumulation (I_{geo}) table, the soils in the studied dumpsites can also be ranked from uncontaminated to moderately contamination with Cu (Table 7) and low risk degree (Table 8). The levels of Cu observed in this present study was higher than the concentration levels of Cu reported for soils around some other selected waste dumpsites or contaminated sites: Nwajei *et al.* (2014) reported on the concentration levels of Cu in soils and vegetation around selected waste dumpsites in Delta State, with mean concentration levels of Cu in soils ranging from 0.52 ± 0.37 to 25.78 ± 15.05 mg/kg; Iwegbue *et al.* (2013) also reported on the concentration levels of Cu ranging from 3.7 to 29.5 mg/kg in soils around cassava processing mills in sub-urban areas of Delta State, southern Nigeria. However, higher levels of Cu

have also been reported in other contaminated sites: Ololade, (2014) reported heavy metal contamination in auto-mechanic workshops in Ikare Akoko, Ondo State, Nigeria with Cu concentration levels ranging from 186.7 to 363.3 mg/kg. Oguntimehin and Ipinmoroti, (2008) reported Cu levels of 151.4 mg/kg in soils from automobile workshops Akure, Nigeria. Tripathi and Mira, (2012) reported Cu mean levels ranging from 14.96 ± 96 to 90.70 ± 1.84 mg/kg in contaminated soils of municipal waste dumpsites at Allahbad, India. Ogbonna *et al.* (2009) reported Cu concentration levels ranging from 24.36 to 68.14 mg/kg in soils of waste dumpsites in Port Harcourt Municipality and Environs and Ojo *et al.* (2012) also reported Cu levels ranging between 37.20 and 120.00 $\mu\text{g/g}$ in soils of major domestic waste dumpsites in Akure, Nigeria.

Table 2: Mean levels of total heavy metals content of aggregate soil samples around dumpsite (I)

Metals (mg/kg)	Located spots in the studied dumpsite							Control X	WHO limit (ppm)
	A	B	C	D	E	F			
Cu	8.30±0.44	8.27±0.06	9.96±0.04	9.23±0.15	8.30±0.26	9.73±0.15	5.23±0.32	100	
Pb	2.03±0.15	2.80±0.00	2.70±0.00	3.30±0.00	5.60±0.00	4.33±0.01	1.70±0.17	200	
Mn	4.59±0.09	5.17±0.15	3.37±0.21	3.17±0.12	5.23±0.21	4.97±0.21	1.10±0.17	3000	
Ni	3.40±0.00	5.13±0.06	3.53±0.15	2.23±0.06	2.09±0.18	3.34±0.09	0.87±0.21	60	
Zn	17.04±0.27	16.49±0.03	9.76±0.05	11.24±0.21	14.08±0.17	23.17±0.06	3.97±0.15	300	
Cd	5.90±0.00	2.93±0.02	3.82±0.07	5.14±0.05	6.24±0.06	6.79±0.02	1.00±0.00	0.6	
Cr	1.23±0.05	1.41±0.01	0.91±0.01	1.06±0.01	1.49±0.01	2.06±0.02	1.17±0.06	100	

The values are Mean ± S.D

Table 3: Mean levels of total heavy metals contents of aggregate soil samples around dumpsite (II)

Metals (mg/kg)	Located spots							Control X	WHO limit (ppm)
	G	H	I	J	K	L			
Cu	23.80±0.08	37.27±0.06	29.30±3.39	17.47±0.21	13.1±0.15	23.23±0.32	5.23±0.32	100	
Pb	8.30±0.00	5.17±0.12	2.90±0.00	6.60±0.00	3.70±0.0	2.00±0.00	1.70±0.17	200	
Mn	9.27±0.31	8.03±0.21	3.77±0.21	5.67±0.12	2.13±0.15	1.57±0.12	1.10±0.17	3000	
Ni	3.57±0.31	4.50±0.00	2.00±0.00	2.53±0.42	1.93±0.12	1.03±0.06	0.87±0.21	60	
Zn	37.93±0.87	30.37±1.01	18.93±0.06	12.20±0.17	12.13±0.32	7.57±0.15	3.97±0.15	300	
Cd	3.27±0.15	5.07±0.15	2.27±0.15	2.13±0.15	1.53±0.15	1.00±0.00	1.00±0.00	0.6	
Cr	5.60±0.36	2.60±0.00	3.43±0.25	1.60±0.17	1.97±0.15	1.37±0.12	1.17±0.06	100	

The values are Mean ± S.D

Table 4: Mean levels of total heavy metals contents of aggregate soil samples around dumpsite (III)

Metals (mg/kg)	Located Spots							Control X	WHO limit (ppm)
	M	N	O	P	Q	R			
Cu	12.40±0.46	29.03±0.25	23.17±0.21	7.63±0.06	14.40±0.00	9.37±0.13	5.23±0.32	100	
Pb	1.43±0.23	3.13±0.12	3.63±0.21	1.23±0.21	3.03±0.06	2.30±0.00	1.70±0.17	200	
Mn	1.30±0.26	2.57±0.15	2.10±0.00	1.53±0.21	2.17±0.21	1.97±0.06	1.10±0.17	3000	
Ni	1.53±0.15	2.07±0.06	1.53±0.21	1.00±0.00	1.70±0.00	1.87±0.12	0.87±0.21	60	
Zn	6.93±0.21	8.83±0.15	11.47±0.25	5.00±0.17	8.93±0.15	5.57±0.06	3.97±0.15	300	
Cd	1.83±0.15	2.53±0.21	2.03±0.06	1.00±0.00	2.17±0.15	3.90±0.00	1.00±0.00	0.6	
Cr	1.40±0.00	2.83±0.15	2.63±0.15	1.13±0.12	1.83±0.12	1.90±0.17	1.17±0.06	100	

The values are Mean ± S.D

Table 5: Mean contamination /pollution index (C/PI) of heavy metals

Metals	Dumpsite (I) mean and (range)	Dumpsite (II) mean and (range)	Dumpsite (III) mean and (range)
Cu	0.25 (0.23 – 0.28)	0.67 (0.37 – 1.04)	0.44 (0.21 – 0.81)
Pb	0.04 (0.02 – 0.07)	0.06 (0.02 – 0.10)	0.03 (0.01 – 0.04)
Mn	0.005 (0.004 – 0.006)	0.006 (0.02 – 0.01)	0.002 (0.002 – 0.003)
Ni	0.10 (0.06 – 0.15)	0.08 (0.03 – 0.13)	0.05 (0.03 – 0.06)
Zn	0.11 (0.07- 0.17)	0.14 (0.05 – 0.27)	0.06 (0.04 – 0.08)
Cd	6.42 (3.66 – 8.49)	3.18 (1.25 – 6.34)	2.81 (1.25 – 4.88)
Cr	0.01 (0.009 – 0.02)	0.03 (0.01 – 0.06)	0.02 (0.01 – 0.03)

Significance: C/PI values greater than unity (>1) defines the pollution range and when lowers than unity (<1) defines the contamination range.

Table 6: Mean heavy metal contamination factors (CF) and pollution load index (PLI)

Metals	Dumpsite (I) mean and (range)	Dumpsite (II) mean and (range)	Dumpsite (III) mean and (range)	Control background mean concentration
Cu	1.71 (1.58 – 1.87)	4.60 (2.51 – 7.13)	3.06 (1.46 -5.55)	5.23 ± 0.32
Pb	2.04 (1.19 – 3.29)	2.81 (1.18 – 4.88)	1.45 (0.72 – 2.14)	1.70 ± 0.17
Mn	4.01 (2.88 ± 4.75)	4.61 (1.43 – 8.43)	1.76 (1.18 – 2.34)	1.10 ± 0.17
Ni	3.78 (2.40 – 5.90)	2.98 (1.18 – 5.17)	1.86 (1.15 – 2.38)	0.87 ± 0.21
Zn	3.85 (2.46 – 5.84)	5.00 (1.91 – 9.55)	1.96 (1.26 – 2.89)	3.97 ± 0.15
Cd	5.14 (2.93 – 6.79)	2.55 (1.00 – 5.07)	2.24 (1.00 – 3.90)	1.00 ± 0.00
Cr	1.16 (0.78 – 1.76)	2.36 (1.17 – 4.79)	1.67 (0.97 – 2.42)	1.17 ± 0.06
PLI	2.76 (1.85 – 3.82)	3.41 (1.41 – 6.19)	1.95 (1.08 – 2.92)	

Significance: Pollution load index (PLI) < 1 denote perfection; PLI = 1 means that only baseline levels of pollutants are present and PLI > 1 would indicate deterioration of site quality.

Table 7: Mean Index of Geo-accumulation (I_{geo} classⁿ) classes of the heavy metals in soils around the dumpsites studied with respect to the natural background

Metals	Dumpsite I	Dumpsite II	Dumpsite III
	Mean and (range)	Mean and (range)	Mean and (range)
Cu	0.34 (0.31 – 0.38)	0.91 (0.50 – 1.41)	0.61 (0.29 – 1.10)
Pb	0.41 (0.24 – 0.66)	0.57 (0.24 – 0.98)	0.29 (0.17 – 0.43)
Mn	0.81 (0.58 – 0.95)	0.93 (0.29 – 1.69)	0.36 (0.24 – 0.47)
Ni	0.76 (0.48 – 1.18)	0.60 (0.24 – 1.04)	0.39 (0.23 – 0.58)
Zn	0.77 (0.49 – 1.17)	1.01 (0.38 – 1.92)	0.39 (0.25 – 0.58)
Cd	1.03 (0.59 – 1.36)	0.51 (0.20 – 1.05)	0.45 (0.20 – 0.78)
Cr	0.23 (0.16 – 0.35)	0.47 (0.23 – 0.96)	0.34 (0.19 – 0.49)

Significance: I_{geo} values > 5, extremely contaminated; 4.5, strongly to extremely strongly contaminated; 3-4, strongly contaminated; 2-3, moderately to strongly contaminated; 1-2, moderately contaminated; 0-1, uncontaminated to moderately contaminated; <0, practically uncontaminated (Tomlinson *et al.*, 1980; Selvaraj *et al.*, 2004; Reddy *et al.*, 2004)

Table 8: The mean metal potential Ecological risk index of a single element (E_R^I) and comprehensive potential Ecological index (RI)

Metal	Dumpsite (I)	Dumpsite (II)	Dumpsite (III)
	mean & (Range)	Mean & (Range)	Mean & (Range)
Cu	8.55 (7.90 – 9.35)	23.00 (12.55 – 35.5)	15.30 (7.30 – 27.75)
Pb	10.20 (5.95 – 16.45)	14.05 (5.90 – 24.40)	7.25 (3.60 – 10.70)
Mn	4.01 (2.88 – 4.75)	4.61 (1.43 – 8.43)	1.76 (1.18 – 2.34)
Ni	18.90 (12.00 – 29.50)	14.90 (5.90 – 25.85)	9.30 (5.75 – 11.90)
Zn	3.85 (2.46 – 5.84)	5.00 (1.91 – 9.55)	1.96 (1.26 – 2.89)
Cd	154.20 (87.90 – 203.70)	76.50 (30.00 – 152.10)	67.20 (30.00 – 117.00)
Cr	2.32 (1.56 – 3.52)	4.72 (2.34 – 9.58)	3.34 (1.94 – 4.84)
RI	202.03 (120.65 – 273.11)	142.78 (60.03 – 265.41)	106.11 (51.03 – 177.42)

Significance: $E_R < 30$, slight pollution; $30 \leq E_R < 60$, medium pollution; $60 \leq E_R < 120$, strong pollution; $120 \leq E_R < 240$, very strong pollution; $E_R \geq 240$, extremely strong pollution. $RI < 40$, slight risk degree; $40 \leq RI < 80$, medium risk degree; $80 \leq RI < 160$, strong risk degree; $160 \leq RI < 320$, very strong and $RI \geq 320$, extremely strong risk degree ((Jiang *et al.*, 2014)

3.2. Lead (Pb)

The overall mean concentration levels of Pb ranged between 1.23 ± 0.21 and 8.30 ± 0.00 mg/kg in soils from the studied dumpsites while the mean levels in soils from the control site was 1.70 ± 0.17 mg/kg (Tables 2-4). The levels of Pb in the studied sites were lower than standards set by CEC (1986), with upper limit of

300 mg/kg and maximum tolerable levels proposed for Agricultural soil, (90-400 mg/kg) set by WHO (1993) and NEPCA (2010). The levels of Pb observed in this present study were higher than the concentration levels of Pb reported for soils around some selected waste dumpsites across the country: Eneje and Lemoha, (2012) reported Pb concentration levels ranging from 0.22 to 1.12 mg/kg in municipal solid waste dump soils in Owerri Imo State, Nigeria. However, higher levels of Pb have also been reported in most contaminated sites: Anake *et al.* (2009) reported Pb mean levels ranging between 169 ± 113 and 2917 ± 538 mg/kg in soils from municipal solid waste dumpsites in Kano and Kaduna State, Nigeria; Nwajei *et al.* (2014) reported Pb mean levels ranging between 44.33 ± 42.55 and 89.62 ± 23.09 mg/kg in Delta State, Nigeria; Amos-Tautua *et al.* (2014) reported Pb mean levels ranging from 14.75 ± 0.0 to 16.14 ± 0.04 mg/kg in surface soils of municipal open waste dumpsites in Yenagoa, Nigeria; Tripathi and Misra, (2012) reported Pb mean levels ranging between 71.47 ± 3.34 and 108.85 ± 3.99 mg/kg in contaminated soils of municipal waste dumpsites at Allahabad, India; Oguntimehin and Ipinmoroti, (2008) reported Pb concentration levels varying between 98.58 and 218.78 mg/kg in soils around automobile mechanic workshops in Akure Ondo State, Nigeria; Ololade, (2014) reported Pb concentration levels ranging between 96.6 and 199.3 mg/kg in soils within auto-mechanic workshops in Ikare Akoko, Ondo State, Nigeria; Oladunni *et al.* (2013) also reported mean levels of Pb in the dry season ranging from 569.07 ± 0.11 to 630.07 ± 0.01 mg/kg and in the wet season, the mean levels ranged between 428.12 ± 0.01 and 502.12 ± 0.12 mg/kg in soils around electronics waste dumpsites in Alaba International Market, Lagos. With respect to contamination / pollution index, the soils from the studied dumpsites can be ranked from very slightly contaminated to slightly contamination with Pb (Table 5). The geo-accumulation index (I_{geo}) also ranked the soils from the studied dumpsites as uncontaminated with Pb (Table 7). Lead contamination of soils are usually from automobile exhaust fumes as well as dry cell batteries, sewage effluents, run off of wastes and atmospheric depositions owing to the close proximity of sites to high vehicular traffic.

3.3. Manganese (Mn)

The mean concentration levels of Mn in soils in the studied dumpsites varied between 1.30 ± 0.26 and 9.27 ± 0.31 mg/kg, the control soil has a mean value of 1.10 ± 0.17 mg/kg (Tables 2-4). It was observed that the Mn in the studied dumpsites was considered anthropogenic when compared with the amount present in the control soils (very low in control concentration level). The contamination / pollution index of Mn in the studied dumpsites soils was ranked very slightly contaminated with Mn (Table 5), with contamination factor (CF) ranging from 1.18 – 8.43 in the studied dumpsites (Table 6). However, Mn index of geo-accumulation was ranked from uncontaminated to moderately contamination in the studied dumpsites (Table 7). Higher levels of Mn in soils that have received significant impact of crude oil in Southern Nigeria have been reported by Iwegbue *et al.* (2009). However, Iwegbue *et al.* (2013) also reported higher levels of Mn in soils around Cassava Processing Mills in sub-urban areas of Delta State, southern Nigeria, with concentration levels varying from 0.1 to 383.2mg/kg. Mn and Ni are fuel additives especially in burning fuel (diesel) that are used in operating heavy duty machines (Sheppard *et al.*, 2000; El-Hassan *et al.*, 2006).

3.4. Nickel (Ni)

The mean levels of Ni in soils in the studied dumpsites ranged from 1.00 ± 0.00 to 5.13 ± 0.06 mg/kg and the control soils had a mean concentration of 0.87 ± 0.2 mg/kg (Tables 2-4). The maximum range of Ni mean levels in the studied dumpsites was far lesser than the Target value (35 mg/kg) of the DPR (2002) for soil heavy metal contamination/pollution limits. The mean concentration levels of Ni found in soils around the studied dumpsites were similar to the mean levels of Ni in soils from municipal solid waste dumpsites in Kano and Kaduna State as reported by Anake *et al.* (2009) with Ni concentration levels ranging from 0.39 – 9.10 mg/kg. However, the levels of Ni recorded in this study were relatively low when compared with the concentration levels of Ni reported in other contaminated sites: Nwajei *et al.* (2014) reported mean concentration levels of Ni ranging from 9.61 ± 7.73 to 23.93 ± 13.08 mg/kg in Agbor, Sapele and Warri in

Delta State, Nigeria. Oguntimehin and Ipinmoroti, (2008) reported Ni concentration level of 62.10 mg/kg in automobile workshops in Akure, Nigeria. Iwegbue *et al.* (2013) reported Ni concentration levels ranging from 4.0 to 11.3 mg/kg in soils around cassava processing mills in sub-urban areas of Delta State, southern Nigeria: Tripathi and Misra, (2014) reported mean concentration levels of Ni ranging between 63.35 ± 2.86 and 92.22 ± 2.04 mg/kg in contaminated soils of municipal waste dumpsites at Allahabad, Uttar Pradesh, India. Ololade, (2014) reported Ni concentration levels ranging from 7.9 to $57.8 \mu\text{g g}^{-1}$ in soils within auto-mechanic workshops in Ikare Akoko, Ondo State, Nigeria. Ojo *et al.* (2012) reported Ni concentration levels ranging between 15.60 and 19.20 $\mu\text{g/g}$ in soils of major domestic waste dumpsites in Akure, Nigeria; Omuku *et al.* (2012) reported Ni concentration levels varying from 14.54 – 35.80 mg/kg with mean levels of 24.69 ± 0.003 mg/kg in soils within New Auto Spare Parts, Nkpor–Agu, Anambra state, Nigeria while Oladunni *et al.* (2013) also reported concentration levels of Ni ranging between 82.70 ± 0.06 and 85.43 ± 0.02 mg/kg in dry season, and the mean levels in the wet season ranged between 80.24 ± 0.75 and 84.24 ± 0.12 mg/kg inside electronic waste dumpsite in Alaba International Market Lagos, Nigeria. With respect to contamination / pollution index, the soils around the studied waste dumpsites could be ranked from very slightly contaminated to slight contamination with Ni (Table 5), with contamination factor ranging between 1.15 – 5.90 (Table 6) while the geo-accumulation index (I_{geo}) of Ni could also be ranked as uncontaminated to moderately contamination with Ni in soils around the studied dumpsites (Table 7).

3.5. Zinc (Zn)

Zinc was ranked as the most abundant heavy metal in this present study. The mean concentration levels of Zn spanned from 5.00 ± 0.17 to 37.93 ± 0.87 mg/kg in soils around the studied dumpsites. The control soils had mean Zn concentration of 3.97 ± 0.15 mg/kg (Tables 2- 4). The solubility of Cu and Zn ions is governed by pH and redox conditions. In the pH range of 5.4 – 6.5, Cu and Zn are distinctly more soluble under oxidizing conditions than reducing conditions. This could be related to their high abundance both in control and in studied dumpsites (Bhattacharya *et al.*, 2002). The contamination factor (CF) of Zn in soils around the studied dumpsites ranged between 1.26 and 9.55 (Table 6). The levels of Zn in soils in the studied dumpsites fits into the ranges of very slightly contaminated to moderate contamination from contamination/pollution index table (Table 5), and with low ecological risk degree (Table 8). However, higher concentration levels of Zn have been reported in some other contaminated sites in Nigeria: Ogbonna *et al.* (2009) reported Zn concentration levels ranging between 10.32 and 128.16 mg/kg in soils from waste dumpsites in Port Harcourt Municipality and Environs: Ojo *et al.* (2012) also reported Zn levels ranging from 320.40 to 441.00 $\mu\text{g/g}$ in soils of major domestic waste dumpsites in Akure, Nigeria: Ololade, (2014) then reported Zn concentration levels spanning between 179.9 and $253.9 \mu\text{g g}^{-1}$ in soils within auto-mechanic workshops in Ikare Akoko, Ondo State, Nigeria: Iwegbue *et al.* (2013) also reported Zn concentration levels ranging between 21.9 to 97.3 mg/kg in soils around cassava processing mills in sub-urban areas of Delta State, southern Nigeria: Oguntimehin and Ipinmoroti, (2008) also reported mean concentration levels of Zn ranging from 328.31 to 693.39 mg/kg in soils from automobile workshops in Akure, Nigeria.

3.6. Cadmium (Cd)

The mean levels of Cadmium in soils around the studied dumpsites ranged between 1.00 ± 0.00 and 6.79 ± 0.02 mg/kg while soil samples from the control site had a mean value of 1.00 ± 0.00 mg/kg (Tables 2 - 4). The mean levels of Cd recorded in the studied sites were having concentration levels higher than the Target limit (0.8 mg/kg) of the DPR (2002). The maximum range of Cd in the studied dumpsites was higher than the natural limits of 0.01 – 3.0 mg/kg in soils as given by MAFF (1992) and CEC (1986). However, the mean levels of Cd in this study is in agreement with the results obtained from other similar study reported by Anake *et al.* (2009), with Cd concentration levels ranging from 0.30 to 4.8 mg/kg in soils from municipal solid waste dumpsites in Kano and Kaduna states, Nigeria: Nwajei *et al.* (2004) also reported Cd mean concentration levels varying from 2.22 ± 1.03 to 3.83 ± 0.43 mg/kg dry weight, in soils around selected

waste dumpsites in Delta state, Nigeria. With respect to contamination / pollution index evaluated in this study, Cd has a range of 1.25 – 8.4 and was ranked from slightly polluted to very severe pollution on the studied dumpsites soils (Table 5). The Cd contamination factors (CF) varied between 1.00 and 6.79 (Table 6) while its geo-accumulation index (I_{geo}) could also be ranked from uncontaminated to moderately contamination with Cd in soils around the studied dumpsites (Table 7). In terms of ecological risk index, Cd varied from strong pollution to very strong pollution with high ecological risk degree (Table 8). However, the mean levels of Cd in this study were found to be higher in concentration than the Cd levels reported in other contaminated sites: Amos-Tauta *et al.* (2014) reported that Cd concentration levels was in trace amount, with mean values of $<0.0001 \pm 0.01$ mg/kg in soils from municipal open waste dumpsites in Yenagoa, Nigeria; Ojo *et al.* (2012) reported Cd mean concentration levels ranging between 1.76 and 2.55 $\mu\text{g/g}$ in soils of major domestic waste dumpsites in Akure, Nigeria; Iwegbue *et al.* (2013) also reported Cd mean concentration levels varying from 0.01 to 1.60 mg/kg in soils around cassava processing mills in sub-urban areas of Delta State, southern Nigeria. Higher concentration levels of Cd have also been reported in other contaminated sites: Ololade, (2014) reported Cd mean levels spanning from 40.8 to 63.4 $\mu\text{g/g}$ in soils within auto-mechanic workshops in Ikare Akoko, Ondo State, Nigeria; Oladunni *et al.* (2013) also reported Cd mean concentration levels ranging between 9.63 ± 0.07 and 9.99 ± 0.07 mg/kg in dry season while in the wet season, the mean levels ranged between 7.28 ± 0.02 to 7.82 ± 0.02 mg/kg in soils within and around electronics waste dumpsites in Alaba international market in Lagos, Nigeria; Ogbonna *et al.* (2009) reported Cd mean levels ranging from 2.16 to 15.46 mg/kg in soils from waste dumpsites in Port Harcourt Municipality and Environs; Tripathi and Misra, (2012) also reported higher Cd mean concentration levels of 35.50 ± 0.89 mg/kg in contaminated soils of municipal waste dumpsites at Allahabad, India. Other contaminated sites were higher concentration levels of Cd have been reported: Bamgbose *et al.* (2000), reported heavy metal pollution in dumpsite of Abeokuta City, Nigeria; Oviasogie and Omoruyi, (2007), also reported levels of heavy metals and physicochemical properties of soil in a Foam manufacturing industry in Benin City, Nigeria; Iwegbue *et al.* (2006b), reported preliminary assessment of metal levels of soil of an oil field in the Niger Delta, Nigeria. Like zinc, Cadmium is found in lubricating oil as part of many additives. It was reported that Cd concentration levels in Car tyres was in the range of 20 – 90 $\mu\text{g/g}$ as Cd contamination in the process of Vulcanization (Jaradat and Momani, 1999). The continuous accumulation of Cd in soils around waste dumpsites may lead to increased uptake of the metal by plants.

3.7. Chromium (Cr)

The mean levels of Cr recorded in soil samples around the studied dumpsites varied between 0.91 ± 0.01 and 5.60 ± 0.36 mg/kg while the mean concentration in control site was 1.17 ± 0.06 mg/kg (Tables 2-4). This implies that most of the Cr present in soils around the studied dumpsites was from anthropogenic origin. The levels of Cr in the studied sites were far lower than the Target limit (100 mg/kg) set by DPR (2002) for contaminated / polluted soil. The mean levels of Cr observed in this study from the studied sites were far lower than the critical permissible limit which is 50 mg/kg for soils recommended for Agriculture by MAFF (1992) and CEC (1986). With respect to contamination / pollution index, the levels of Cr in this study could be ranked as very slightly contaminated (Table 5), with contamination factor ranging between 0.78 and 4.79 (Table 6). The geo-accumulation index of Cr was also ranked from uncontaminated to moderately contamination (Table 7), with low ecological risk degree (Table 8). However, the levels of Cr in this present study agrees with the findings of Nwajei *et al.* (2014), who investigated the heavy metals concentration levels in soils and vegetation around selected waste dumpsites in Delta state, Nigeria. Lower concentration levels of Cr have also been reported in some contaminated sites across the country: Amos-Tautua *et al.* (2014) reported on Cr concentration levels ranging from 0.05 ± 0.01 to 0.06 ± 0.01 mg/kg in surface soils of municipal open waste dumpsite in Yenagoa, Nigeria. Iwegbue *et al.* (2013) also reported mean concentration levels of Cr ranging between 0.01 and 3.70 mg/kg in soils around cassava processing mills in sub-urban areas of Delta State, southern Nigeria. Higher levels of Cr have been reported also in other contaminated sites across the country. Anake *et al.* (2009) reported Cr mean concentration levels varying from 7.20 ± 1.49

to 81.20 ± 61.30 mg/kg in soils at municipal solid waste dumpsites in Kano and Kaduna states, Nigeria. Ololade, (2014) also reported Cr mean concentration levels ranging between 52.3 and $74.5 \mu\text{g g}^{-1}$ in soils within auto-mechanic workshops in Ikare Akoko, Ondo State, Nigeria. Oguntimehin and Ipimoroti, (2008) reported Cr concentration levels spanning from 28.50 to 115.03 mg/kg in soils from automobile workshops in Akure, Nigeria. Oladunni *et al.* (2013) also reported Cr mean concentration levels ranging between 19.11 ± 0.01 and 46.58 ± 0.02 mg/kg in soils around an electronic waste dumpsite, Alaba international market in Lagos, Nigeria. Ojo *et al.* (2012) reported Cr mean concentration levels varying between 17.06 and 22.10 $\mu\text{g/g}$ in soils of major domestic waste dumpsites in Akure, Nigeria. Iwegbue *et al.* (2006b) also reported high levels of Cr in the preliminary assessment of metals levels of soil of an oil field in the Niger Delta, Nigeria. Sources of Cr in the soils could be due to waste consisting of coloured polythene bags, lead-chromium batteries, discarded plastic materials and empty paint containers (Amos–Tautua *et al.*, 2014).

The analytical ANOVA (Table 9) of the analysed heavy metals from the studied sites showed that there is significant difference ($P \leq 0.05$) between the mean heavy metal concentration levels in the control soils and the soils around the studied dumpsites. The soils around dumpsites II (D2) had the highest heavy metal mean concentration levels with the exception of Ni and Cd levels in dumpsite I (D1), were both also had the highest mean concentration levels. The coefficient of variation (CV) of the analysed heavy metals from the studied sites in this study could be ranked high in variation with Zn concentration levels having the highest variation of 56% and Ni with the least coefficient of variation (35%) (Table 9). The Pearson's correlation matrix (Table 10) showed that the analysed heavy metals were positively and significantly correlated with one another. Therefore, there is a conclusion that positive correlation between heavy metals is an indication of common sources, mutual dependence and identical behaviour during transport (Rodriguez *et al.*, 2008).

Table 9: The ANOVA comparison of the mean heavy metals in the studied site using the least significance difference (LSD) *t*-test at $P \leq 0.05$ for mean separation

Parameters	D ₁	D ₂	D ₃	X _s	GM	V(±)	P-value (≤0.05)	LSDM (0.05)	SEM (±)	SEDM (±)	CV (%)
Cu	8.97	24.03	16.00	5.23	13.60	26.49	0.001**	6.33	2.10	2.97	38
Pb	3.46	4.78	2.46	1.70	3.10	2.59	0.02**	1.98	0.66	0.93	52
Mn	4.42	5.07	1.94	1.10	3.13	2.79	0.002**	2.06	0.68	0.97	53
Ni	3.29	2.59	1.62	0.87	2.09	0.52	0.001**	0.89	0.29	0.42	35
Zn	15.30	19.86	7.79	3.97	11.70	42.70	0.003**	8.04	2.67	3.77	56
Cd	5.14	2.55	2.24	1.00	2.73	1.58	0.001**	1.55	0.51	0.73	46
Cr	1.36	2.76	1.93	1.17	1.81	0.83	0.03*	1.12	0.37	0.53	50

There is significant difference at $P \leq 0.05$ between control and the dumpsites. Significant; ** = $p < 0.05$, * = $p < 0.05$, where D₁ = dumpsite (I) mean, D₂ = dumpsite (II) mean, D₃ = dumpsite (III) mean, X_s = control mean, GM = Grand or total mean, V = variance with 15 degree of freedom, LSDM = Least significant difference of means (5% level), SEM (±) = Std. Errors of Means, SEDM (±) = Std. Errors of difference of means, CV(%) = Coefficient of variation.

Table 10: Significant Correlation between mean heavy metals of soils around the studied dumpsites

	Cu	Pb	Mn	Ni	Zn	Cd	Cr
Cu	1.000						
Pb	0.485	1.000					
Mn	0.506	0.859	1.000				
Ni	0.352	0.536	0.823	1.000			
Zn	0.587	0.786	0.935	0.762	1.000		
Cd	0.130	0.458	0.635	0.667	0.585	1.000	
Cr	0.682	0.682	0.626	0.334	0.760	0.146	1.000

4. CONCLUSION

The results from this study have allowed the analysis of the levels of some toxic heavy metals in soils around municipal solid waste dumpsites in Benin City. The combined use of different approaches for evaluating soil heavy metal contamination and pollution facilitates a comprehensive interpretation of the soil characteristics in terms of the background influences. The levels of heavy metals like Cu, Pb, Ni, Mn, Zn, and Cr in soils around the studied dumpsites were lower than the DPR target values with the exception of Cd that was far higher than the target values. The contamination / pollution index of the analysed heavy metals from this study showed that the studied heavy metals were in the contamination ranges with low risk degree, with the exception of Cd that was in the pollution ranges with high risk degree as also indicated by the potential ecological risk index. The heavy metals pollution load index (PLI) of the studied dumpsites was low. The mean concentration levels of the analysed heavy metals around the studied waste dumpsites were also lower than the permissible limits set by WHO and FAO for agricultural purpose except Cd. But the prolong accumulation of these heavy metals in the soil could pose environmental risk. Anthropogenic wastes and urbanization activities could account for the high levels of some of the potential toxic heavy metals observed in this study.

5. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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